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Processes Affecting the Transport of Arsenic in the  
Madison and Missouri Rivers, Montana

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A Report to Montana Water Resources Center  
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MONTANA DEPT. OF NATURAL RESOURCES

by

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## Abstract

A study conducted by Stauffer et al. (1980), on hot-spring drainages of Yellowstone National Park, established a considerable source of arsenic and other natural contaminants in the headwaters of the Madison River. Sediment and water samples collected from the Madison and Missouri Rivers (Hebgen Lake to Canyon Ferry Reservoir) are enriched in arsenic suggesting that the Madison River headwaters supply arsenic throughout the drainage. HCl-extractable arsenic was weakly correlated with iron, manganese, aluminum, and organic carbon suggesting little control of water-column arsenic by these constituents. Sediment arsenic concentrations of the upper Missouri River are within a range predicted by a sediment mixing model indicating that dilution is playing a prominent role in the observed arsenic trend. Water-column arsenic was strongly correlated with dissolved sodium suggesting that arsenic behaves conservatively in the drainage and supporting a dissolved phase for arsenic transport. Water-column arsenic was weakly correlated with iron, aluminum, and manganese suggesting little control by colloids ( $<0.45$  micron) of these metals. Sediment core samples collected from Ennis Lake suggest that diagenetic cycling is the process by which arsenic is concentrated in the surface sediments (0 to 10 cm interval). If anerobic conditions periodically prevail in the Ennis Lake water column then arsenic may be mobilized as iron and manganese oxyhydroxides are reduced. This may explain the water-column arsenic concentrations which are elevated in all Madison River lakes.

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**Processes Affecting the Transport of Arsenic in the  
Madison and Missouri Rivers, Montana**

## Introduction

The upper Missouri River drainage, located in Southwest Montana, receives significant inputs of arsenic and other natural contaminants from geothermal areas in the headwaters of the Madison River located in Yellowstone National Park (Stauffer et al., 1980). Downstream, the Missouri River, which is formed by the confluence of the Madison, Jefferson and Gallatin Rivers, has been shown to contain arsenic at levels in excess of background (Knapp and Horpstead, 1987; Knapp and Brosten, 1987). Irrigation and other surface water uses have resulted in arsenic contamination of the alluvial aquifers of the lower Madison Valley (Sonderegger and Sholes, 1989; Sonderegger et al., 1989; Sonderegger and Ohguchi, 1988). This work, while suggesting that arsenic travels long distances, does not provide any data on the distribution, mobility, or behavior of arsenic in the Madison and Missouri Rivers.

Although the regional distribution of arsenic from natural sources has not been studied, much is known about the geochemistry of arsenic in natural systems. The mobility of arsenic in any aquatic system is strongly controlled by changes in the redox conditions of the sediment (Fuller and Davis, 1990; Moore et al., 1988). In oxic environments arsenic is stabilized through adsorption by hydrous iron oxides (Mok and Wai, 1988, 1990; Cherry et al., 1986; Brannon and Patrick, 1987). Conversely, reducing environments mobilize arsenic because of the reduction of ferric-oxides to release ferrous iron (Drever, 1988; Ferguson and Gavis, 1972; Stauffer et al., 1980). Lake and stream sediment is usually oxidized to a shallow depth. However, with increasing depth, a reducing environment

prevails due to the decay of organic matter (Drever, 1988; Ferguson and Gavis, 1972; Aggett and O'Brien, 1985). If the local aquifer recharges through these sediments contamination of the groundwater can result (Moore et al., 1988).

The mobility of arsenic is also controlled by adsorption onto aluminum and manganese oxides. Under neutral to mildly acidic conditions, aluminum oxides have been shown to be an important scavenger of dissolved arsenate (Logsdon et al., 1974; Gupta and Chen, 1978; Anderson, et al., 1976). In lake sediments arsenic has been shown to be strongly correlated with manganese, presumably as a result of diagenetic cycling similar to that of iron (Peterson and Carpenter, 1985; Takamatsu et al., 1985). All of these processes suggest that the sediment of the Madison and Missouri rivers, as well as the reservoirs located thereon, are likely sinks and sources for arsenic dissolved in the waters.

The present study was undertaken in an effort to understand the relationships between particulate arsenic and other elements (particularly iron, aluminum, and manganese) and determine the processes fixing and transporting arsenic in the Missouri River system from the headwaters of the Madison River to Canyon Ferry Reservoir, 350 river kilometers downstream from the source.

## Methods

Stream sediment and water samples were collected over three periods, December 12-16, 1989, and March 19-20, 1990 from the Missouri, Madison, Jefferson, and Gallatin Rivers, and September 28-29, 1990 from the Firehole, and Gibbon Rivers (Figure 1). Sample locations were chosen on the basis of

accessibility and abundance of fine-grained sediment. River-bed sediment samples were collected over a 7-10 meter reach of river from the upper several centimeters of sediment using a nylon spoon. Many studies (Forstner and Wittman, 1983; Bradford and Horowitz, 1982) describe the importance of minimizing grain size differences between sample locations when analyzing for trace elements. For this reason, each sample was sieved, on site, with river water through a 63  $\mu\text{m}$  mesh nylon screen. The samples were then stored in 250 ml acid-washed plastic bottles (before use the spoon, mesh, 2-piece pvc mesh holder, and bottles were rinsed, on location, with river water).

Water samples were withdrawn from the surface with a 60 cc syringe and injected through a 0.45  $\mu\text{m}$  cellulose triacetate filter into 125 ml acid-washed plastic bottles. Before use the bottles were rinsed, on site, with approximately 50 ml of river water injected through the filter. The bottles were filled to the 100 ml mark and acidified with approximately 300  $\mu\text{l}$  of concentrated nitric acid (Baker Intstra-Analyzed). In addition, surface water pH was measured at each location.

Reservoir sediment samples were collected, using a clamshell dredge, May 9-12, 1990, from 6 locations on Canyon Ferry, 9 on Toston, 10 on Ennis, 3 on Quake, and 12 from Hebgen (Madison Arm) Lakes (Appendix). Water depth at each sample location ranged from less than 1 meter to 3 meters on Canyon Ferry Reservoir to 11 meters on Hebgen Lake. All reservoirs and lakes were below full pool with only Canyon Ferry showing any visible suspended sediment. One water sample was collected from each reservoir/lake, with the exception of Hebgen Lake from which 2 samples were collected. In addition, water samples were collected from 2 tributaries of the Madison River, Wolf and Cabin Creeks

(river km 198 and 240, respectively). All water samples were collected as per the method described above.

All samples were stored on ice following collection and returned to the University of Montana for analyses. Within 24 hr of returning, the sediment samples were centrifuged at 2000 rpm for 10 min, the supernatant decanted, and the samples placed in a deep freeze.

In an effort to ascertain the role of the reservoirs in this system, additional sediment and water samples were collected from Ennis Lake July 16-18, 1991. Sediment cores were collected from approximately the same locations that were chosen for grab samples during May 9-12, 1990 (Figure 26). In addition, 4 bed sediment samples were collected from the Madison River above Ennis Lake over approximately the same locations that were sampled December 12 -16, 1989 (Appendix, sites MA13 - MA16). The corer used was a JMC Back-Saver Handle with a JMC "O" Contamination Tube designed to allow insertion of a 0.90 inch diameter, rigid, acetate, liner tube. At each sample location a clean acetate liner was inserted into the soil corer. After the core was taken, the acetate liner was removed from the corer and the ends sealed with Parafilm "M" laboratory film. Water samples were collected throughout the reservoir (Figure 26) and were drawn from a depth of approximately 1 meter by a peristaltic pump. The samples were passed through 0.45 micron cellulose triacetate filters into 125 ml acid-washed plastic bottles (before use the bottles were rinsed with reservoir water passed through the filter). After approximately 100 ml of sample was collected it was treated with 300  $\mu$ l of concentrated nitric acid (Baker Intstra-Analyzed). At each site the pH, temperature, and dissolved oxygen were measured from water

drawn from the same depth. Prior to sample collection five sites were chosen in order to determine if a hypolimnion existed (Figure 26). The water temperature was measured several centimeters below the surface, and within 10 centimeters of the bottom of the reservoir. The results indicated that no significant stratification existed at the time of sample collection (Appendix). Additional water samples were collected once approximately every 6 hours over a 24 hour period from both above and below Ennis Lake using the method described above for the main stem samples (Figure 27, sites AER and BER). All samples were stored on ice and returned to the University of Montana where they were refrigerated. Within 48 hrs of returning, the sediment samples were extruded from the acetate tubes, cut into 10 cm sections, stored in styrofoam containers, and returned to the refrigerator.

HCl-extractable metals have been shown to approximate the amount of each metal that is available to the environment (Luoma and Davis, 1983; Luoma and Jenne, 1977; Tessier et al., 1979). For this reason an HCl-extraction procedure was performed on all sediment samples. The sediment samples were placed in an oven set at 70 °C and allowed to dry for 24-36 hours (drying time varied due to weight differences between samples). After the samples were dry approximately 0.500 g of each was placed in a centrifuge tube, covered with 40 ml of 0.60 N HCl, and placed on a shaker table for 24 hours. Following this procedure the samples were centrifuged at approximately 2700 rpm for 10 minutes and the supernatant decanted into 40 ml acid washed plastic bottles.

Prior to drying the samples, a subsample of each was used in a wet extract. The extraction procedure used was essentially the same as described above with

the exception of the amount of time each sample spent in the 0.60 N HCl. For the wet sediment extraction procedure the reaction time was approximately 2 hours. In addition, an aliquot of each wet sediment sample was weighed to within two decimal places of the weight of the sample used in the extraction. These aliquots were then dried for approximately 24 hours at 70 °C and re-weighed. The weight of the dried aliquots were then recorded as a surrogate sample weight for the extractions. A comparison of these two methods with respect to the amount of arsenic recovered is presented in figure 2A. The correlation between these two methods is significant and improves by removing the Hebgen and Quake Lake data (Figure 2B). There was no significant difference between the two extraction techniques with respect to the correlations between arsenic and iron, aluminum, and manganese. For this reason data from extracts of dried samples were used.

Additional aliquots of each sediment sample were used for total and carbonate carbon analyses. Each aliquot was analyzed, in duplicate, on an UIC Model 5010 CO<sub>2</sub> Coloumeter with the difference between the two analyses giving the organic carbon content (Appendix). The precision of these methods was established through repeated analysis of experimental grade calcium carbonate.

Both water and HCl-extraction solutions were analyzed with an Inductively Coupled Argon Plasma Spectrometer (Jarrel-Ash Model 800 Atom Comp) to determine the concentration of Al, As, Ca, Fe, Mn, and Na. The accuracy and precision for this method was established through repeated analysis of USGS (United States Geological Survey) water standards T103, T97 (Table 1), and sediment standard SED2, as well as NBS (National Bureau of Standards) sediment standards 1646, and 2704 (Table 3). An additional check of instrument precision



was made through standard additions of 1.00 and 10.00 mg/l arsenic and 100.00 mg/l calcium to previously analyzed samples chosen at random (Tables 2, 4, and 5).

## Results and Discussion

The valence state of arsenic is critical both for its bioavailability and when considering sorption reactions involving amorphous precipitates (Salomons and Forstner, 1988; Pierce and Moore, 1980, 1982; Peterson and Carpenter, 1985). Arsenite forms, As(III), are much more toxic for biological species and more mobile than those of arsenate, As(V) (Ferguson and Gavis 1972). Arsenate has been shown to be more readily adsorbed by iron oxides and the most important species when considering aluminum and manganese oxides (Pierce and Moore, 1980, 1982; Takamatsu et al., 1985; Thanabalasingan et al., 1986). The dominant arsenic species was not determined analytically in this study. However, dissolved oxygen measurements taken hourly over approximately 36 hours near West Yellowstone and Three Forks, MT. (average concentrations were 98% and 96% of total saturation, respectively), and over the sample locations on Ennis Lake (91%), indicate oxidizing conditions, and so relatively high Eh values. This suggests that the dominant arsenic species was most likely arsenate (Figure 3).

### Trends and Relationships in Solutes

All data are presented in figures 4 through 6 and appendix A. These data

must be viewed with caution because of different sampling times for the reservoirs and the upper Madison River and because the amount of seasonal variation is not known.

Arsenic concentrations are elevated in the headwaters of the Madison River and drop significantly between Hebgen and Quake Lakes (Figure 4). Below Quake Lake the arsenic concentrations demonstrate a more gradual decrease to Canyon Ferry Reservoir with all main stem sites elevated over the tributaries. The reservoirs on the Madison River all possess elevated concentrations of arsenic when compared to the main stem sites (Figure 4). As well, sodium and aluminum are elevated in the headwaters of the Madison River (Figures 5A and 5B). However, aluminum concentrations lie primarily at or below the limit of detection from above Quake Lake to Canyon Ferry Reservoir (Figure 5B) while the sodium concentrations display a trend similar to that of arsenic (Figure 5A). Iron and manganese concentrations are low in the upper Madison relative to the concentrations recorded below Hebgen Lake and the Missouri River (Figures 6A and 6B). Below Quake Lake the iron concentrations are highly variable throughout the Madison River and show a moderate increase in the Missouri River (Figure 6A). The manganese concentrations are relatively low throughout the drainage and display no distinct trend (Figure 6B).

Stauffer et al. (1980) reported lower arsenic and higher manganese concentrations in water samples collected from the spillway of Hebgen dam relative to the upper Madison River. They attributed this decrease to inputs from sources other than the Madison River acting to dilute arsenic and increase manganese concentrations in Hebgen Lake. The data collected for this study

shows that the arsenic concentrations drop considerably from the upper Madison to the sites located below Hebgen Lake (Figure 4). Conversely, the manganese concentrations show an increase from the upper Madison to the sites located between Hebgen and Quake Lakes (Figure 6B). All of this suggests that arsenic is being diluted while residing in Hebgen Lake thus corroborating the findings of Stauffer et al. (1980). Arsenic concentrations are elevated in the Madison Arm portion of Hebgen Lake. Because only the Madison Arm was sampled (appendix) these data cannot be considered as being representative of the entire lake. However, these data suggest that some processes may be adding arsenic, at least locally, to the water column.

Scatterplots of Fe, Al, and Mn vs. As for the Missouri and Madison Rivers only (Figures 7A through 7C), show no strong correlations which suggest little control by colloids of these metals ( $< 0.45$  micron). Because a 0.45 micron filter was used to collect all water samples, there exists a possibility that As was adsorbed/coprecipitated with Fe, Al, and Mn colloids. This relationship was tested by an experiment conducted on the Firehole and Gibbon Rivers in which water samples were collected using 0.1, 0.45, and 0.8 micron filter as well as a fourth unfiltered sample. Figures 8A and 8B show that there is no measurable difference in the As and Al concentrations with increasing pore size in both tributaries. However, the Fe and Mn concentrations increase (Figures 9A and 9B) from the 0.1 micron filter to the unfiltered sample (Mn concentrations were below detection in the Firehole River). Because of the lack of any relationship between As, Fe, and Mn oxyhydroxides, these data suggest that colloids are not important and that arsenic is likely carried in true solute form ( $> 0.1$  micron).

Correlations between Na and As are strong over the entire data set (Figure 10A) and remain significant when removing the outliers from Hebgen Lake and the upper Madison (Figure 10B). This relationship between arsenic and a conservative element (Manahan, 1991; Stauffer et al., 1980), strongly suggests that arsenic is behaving conservatively and supports the solute nature of arsenic in the basin.

#### Trends and Relationships in Sediment

The arsenic, metal, organic carbon, and carbonate carbon data are presented in figures 11 through 14 and appendix A. In general, the arsenic concentrations are highly variable in the Madison River and are elevated over the Missouri River and tributary values (Figure 11A). Above Quake Lake the concentrations are low relative to the average value of Hebgen Lake. Below Quake Lake the concentrations are initially elevated before decreasing with distance toward Canyon Ferry Reservoir. Aluminum concentrations display a trend that is similar to that of arsenic (Figure 11B). However, the tributary values are not significantly different from the concentrations found in the lower Madison. Furthermore, the Missouri River aluminum concentrations are generally elevated over the Madison River values. Iron concentrations, like arsenic and aluminum, are relatively low in the upper Madison and show an increase, on average, in Hebgen Lake (Figure 12A). In addition, the iron concentrations increase below Quake Lake before showing an overall decrease with river kilometer toward Canyon Ferry Reservoir. Unlike arsenic and aluminum, iron concentrations do not drop between Hebgen

and Quake Lakes but are similar to both lakes (Figure 12A).

Sodium concentrations are elevated in the headwaters of the Madison River and show an overall decrease with river km to Quake Lake (Figure 12B). From Quake Lake to the headwaters of the Missouri River the concentrations remain relatively constant before showing a moderate decrease below the Jefferson and Gallatin rivers. Manganese and organic carbon concentrations are relatively low throughout the drainage and are at levels in the tributaries similar to those of the main stem (Figures 13A and 13B). Calcium and carbonate carbon concentrations are relatively low throughout the Madison River and increase significantly in the Missouri River (Figures 14A and 14B). The concentrations of these two elements are significantly elevated in the tributaries when compared to the Madison River values.

During the May - June runoff periods, Stauffer et al. (1980), suggests that the pH of the upper Madison River likely drops while the riverborne flux of sorption active clastics increases. In neutral to mildly alkaline solutions, a relatively small decrease in pH has been shown to result in an increase in the amount of arsenate adsorbed by hydrous Fe oxides (Fuller and Davis, 1990; Pierce and Moore, 1982). Therefore, it is possible that dissolved arsenate is being controlled by sorption onto riverborne sediment/particulate during high flow periods. Upon encountering Hebgen Lake the entrained sediments are redeposited. All of this could account for the increase in the average arsenic concentration from the upper Madison to Hebgen Lake (Figure 11A).

The overall decrease in sediment arsenic concentrations from Hebgen Lake to Canyon Ferry Reservoir suggests that dilution may be playing a primary role in

the observed trend (Figure 11A). The Missouri River average arsenic concentration is lower than that observed in the lower Madison River. This is likely the result of further dilution by the relatively arsenic-free sediment of the Jefferson and Gallatin Rivers (Figure 11A).

Fe-Al-Mn-organic carbon/As molar ratios are presented in figures 15A through 16B. Arsenic may behave differently in the lakes and reservoirs of the Missouri and Madison rivers due to the possible existence of anaerobic conditions in their respective water columns. For this reason the data presented is limited to the Missouri and Madison River main stem and tributary sites only. Both the Fe/As and Al/As molar ratios are low and relatively constant when compared to the Missouri River and tributary data (Figures 15A and 15B). Given the large degree of variability in the arsenic concentrations (Figure 11A), the relatively constant ratios found in the Madison River data indicate possible control of arsenic by oxyhydroxides of these metals. The increase in Missouri River Fe/As and Al/As molar ratios (Figures 15A and 15B) are due most likely to dilution of the arsenic enriched Madison River sediments by the sediment of the Jefferson and Gallatin Rivers which are depleted in arsenic (Figure 11A). The variability in the Missouri River molar ratio data suggests little control of arsenic by iron and aluminum oxyhydroxides. In contrast to the Fe/As and Al/As molar ratio data, the Mn/As and organic carbon/As molar ratios are relatively low and highly variable throughout the Madison and Missouri Rivers (Figures 16A and 16B). This indicates little control of arsenic by Mn oxides and organic carbon. However, like Fe/As and Al/As, these ratios increase from the Madison to the Missouri River indicating that dilution may be playing a primary role in the observed sediment

arsenic trends of the Missouri River.

Scatterplots of Fe, Al, Mn, and organic carbon vs. As for the Missouri and Madison Rivers demonstrate no correlation (Figures 17A through 17D). Limiting the data set to the Madison River strengthens the relationships. However, the correlation coefficients are not indicative of a strong or even a modest relationship (Figures 18A through 18D). The scatterplot of Fe vs. As shows the most improvement when limited to the Madison River (Figure 18A). In light of the relatively constant Fe/As molar ratio data (Figure 15A), and the large body of evidence describing arsenic's affinity for iron oxyhydroxides, these data suggest a possible relationship.

The sorption of arsenic onto Fe, Al, and Mn oxyhydroxides has been shown to be strongly dependant upon solution pH (Fuller and Davis, 1990; Pierce and Moore, 1980, 1982; Logsdon et al., 1974; Takamatsu et al., 1985; Oscarson et al., 1980, 1981, 1983; Moore et al., 1989). In general, neutral to mildly alkaline waters are sub-optimal for sorption reactions between arsenic and oxyhydroxides of these metals (Pierce and Moore, 1982; Logsdon et al., 1974; Oscarson et al., 1980, 1981, 1982; Takamatsu et al., 1985). This is related to the point of zero charge of these oxyhydroxides; Fe possessing the highest in the range of 8 - 9, followed by Al and Mn at 7 - 8 and 2 - 3, respectively (Manahan, 1991). Below their respective points of zero charge, these oxyhydroxides acquire positive surface charges, the strength of the charge increasing with decreasing pH (Manahan, 1991). At the time of this study, the measured pH of the Madison and Missouri Rivers was  $8.1 \pm 0.2$  (the Madison River pH above Hebgen Lake was  $7.5 \pm 0.2$ ). All of which may explain the relatively weak relationships between As and Fe, Al,

and Mn.

### Sediment Mixing Model

The elevated calcium concentrations in both the Jefferson and Gallatin Rivers (Figure 14A) provide an opportunity to determine the percent of Missouri River sediment which originates in the Madison River. This is possible because Ca is likely derived from HCl dissolution of  $\text{CaCO}_3$  which is primarily conservative over the pH range recorded at the time of this study (Manahan, 1991; Snoeyink and Jenkins, 1980). Faure (1991) describes this model through the following formula:

$$f_a = (X)_m - (X)_b / (X)_a - (X)_b$$

where  $f_a$  = percent contribution of source A

$(X)_a$  = Concentration of X supplied by source a

$(X)_b$  = Concentration of X supplied by source b

$(X)_m$  = Concentration of X found in a mixture of a and b

Letting X = the average calcium concentration

m = the Missouri River above Toston Reservoir

a = the Madison River below Ennis Lake

b = the Jefferson and Gallatin Rivers combined

The results are presented in table 4 and indicate that the percent contribution by the Madison River is approximately  $42\% \pm 13\%$  and that the Jefferson and Gallatin rivers combined contribute  $58\% \pm 13\%$  (the range of 13% is half the difference between  $f_a$ 's calculated using one standard deviation above and below



the mean values of (X)<sub>a</sub>, (X)<sub>b</sub>, and (X)<sub>m</sub>). A test on the validity of this model can be made by applying it to other elements associated with the sediment which are thought to behave conservatively in this system. One such element is carbonate carbon based on the reasonable assumption that it is associated primarily with CaCO<sub>3</sub> (Drever, 1988; Manahan, 1991). The predicted carbonate carbon concentration for the Missouri River is  $10,111 \pm 2324$  which is in close agreement with the actual concentration of 10,220. Applying this model to the arsenic data yields a predicted average concentration of  $25.3 \pm 7.5$  which is somewhat elevated over the actual average concentration of  $13.1 \pm 7.0$  but within the range of error. This model holds when applied to the remaining elements, Fe, Al, Na, and Mn, and yields predicted concentrations for Fe and Al which are in close agreement with their actual averages (Table 3).

Because both the Jefferson and Gallatin Rivers possess relatively low concentrations of sediment-bound arsenic, this model suggests that the arsenic enriched sediment of the Madison River is being diluted by approximately 60% while residing in the Missouri River above Toston Reservoir and that arsenic trends are primarily controlled by dilution.

#### Ennis Lake Sediment

All data is presented in figures 19A through 24B and the Appendix. The depth profiles for cores 1B, 3B, 4B, and 9B all show the maximum arsenic and manganese concentrations in the 0 - 10 cm interval (Figures 19A through 19D). This shallow depth concentration maxima is observed for iron in cores 3B and 4B

as well (Figures 20A and 20B). All of this suggests either a recent deposition of metal and arsenic enriched sediment or, more likely, diagenetic cycling of these constituents.

The sediment-arsenic concentrations of Ennis Lake are comparable to the observed concentrations of the upper Madison River which does not receive any anthropogenic inputs (Figure 11A). Furthermore, if the elevated surficial arsenic concentrations were derived from anthropogenic sources, then we should also see relatively little change in the concentrations of iron and manganese with depth as these elements are commonly scavenged by sulfides in a reducing environment (Nordstrom, 1982; Moore et al. 1988). All of this suggests that a relatively recent deposition of arsenic and metal rich sediment is not likely.

It is reasonable to assume that the sediment of the Madison River has always been enriched in arsenic due to inputs of arsenic enriched water from hot-spring drainages in Yellowstone National Park (Stauffer et al., 1980). Furthermore, it is likely that Ennis Lake has continuously acted as a trap for sediment since its construction. This suggests that the arsenic maxima found over the 0 - 10 cm interval is due to diagenetic cycling.

Diagenetic cycling involves speciation, dissolution, diffusion, and advection of porewater and arsenic compounds in response to a change in the chemical environment (Takamatsu et al., 1985; Peterson and Carpenter, 1985). With increasing sediment depth a reducing environment prevails due to the consumption of oxygen during organic degradation by microbes (Drever, 1988; Ferguson and Gavis, 1972; Aggett and O'Brien, 1985). With continued sediment deposition the redox boundary gradually moves higher in the sediment column,

thus subjecting previously oxidized sediment to a reducing environment.

Arsenic has been shown to be strongly associated with iron and manganese oxyhydroxides in surficial lake sediments (Takamatsu et al., 1985; Peterson and Carpenter, 1985). As these oxyhydroxides are subjected to a reducing environment, Fe(III) and Mn(IV) are reduced to Fe(II) and Mn(II) which releases them to the porewater (Nordstrom, 1982; Peterson and Carpenter, 1985). This results in the release of As(V) associated with these compounds to the porewater and its subsequent reduction to As(III) (Ferguson and Gavis, 1971). In anthropogenically contaminated systems, sulfides commonly scavenge these elements effectively removing them from the porewater (Nordstrom, 1982; Moore et al., 1988). Lake environments that are largely free of anthropogenically derived contamination are typically low in sulfides (Duel and Swoboda, 1972). With no mechanism to remove arsenic, iron, and manganese from the porewater they likely diffuse or advect upward due to continued sediment loading.

The upward diffusion or advection of Mn(II) and its subsequent oxidation and precipitation likely accounts for the concentration maxima found in the surficial sediments (0 - 10 cm) of cores 1B, 3B, 4B, and 9B (Figures 19A through 19D). Fe(II) oxidizes and precipitates more rapidly than Mn(II) upon encountering dissolved oxygen (Jenne, 1976). This could account for the 10 - 20 cm interval Fe maxima in cores 1B and 9B (Figures 21A and 21B) as opposed to the 0 - 10 cm interval Mn maxima (Figures 19A and 19D). This relationship between iron and manganese in sediment profiles has been reported by researchers working in similar environments (Peterson and Carpenter, 1985). The similarities in the core profiles of Mn and Fe at sites 3B and 4B (Figures 19B, 19C, 20A and 20B) most

likely results from a resolution problem stemming from the fact that the cores were sectioned into 10 cm lengths. Unlike Fe(II) and Mn(II) oxidation, the oxidation of As(III) to As(V) alone, in natural environments, does not directly result in the precipitation of arsenate (Salomons and Forstner, 1988). This suggests that the arsenic maxima found in the 0 - 10 cm interval is likely occurring through adsorption and/or coprecipitation with hydrous Fe and Mn oxides as has been suggested by researchers working in other lake environments (Takamatsu et al., 1985; Peterson and Carpenter, 1985).

A comparison of the Fe and Mn profiles, with respect to arsenic, from cores 1B and 9B (Figures 19A, 19D, 21A, 21B) suggests that Mn may be more effective than Fe at adsorbing or coprecipitating with As at these sites. Hydrous manganese oxide has a point of zero charge of approximately 2.3 while hydrous iron oxide is approximately 8.6 (see Takamatsu et al., 1985; Drever, 1988; Manahan, 1991). At pH values below their respective points of zero charge both oxides acquire positive surface charges. If the porewater pH of cores 1B and 9B was acidic, we should see a strong relationship between iron and arsenic given the relative abundance of iron at these sites as compared to manganese. In their work with lake sediments Takamatsu et al. (1985) found that in the presence of divalent cations, especially Mn(II), hydrous manganese oxides were highly efficient adsorbers of arsenate up to pH 8. This they attributed to the adsorption of divalent cations, by hydrous manganese oxides, which induces a positive surface charge. All of this is a possible explanation for the strong relationship between arsenic and manganese, relative to iron, from cores 1B and 9B but is difficult to substantiate without porewater and species data.

The depth profile of Fe and Mn in core 2B (Figures 22A and 22B) suggests that dissolved oxygen is available to a greater depth than in the other cores. Furthermore, the arsenic concentrations are considerably lower than those observed at the other sites and show a relatively insignificant increase in concentration from the 30 - 40 cm interval to the 20 - 30 cm interval (Figure 22A). Although porewater samples were not collected, this data suggests low porewater arsenic concentrations at this site relative to the other locations which may be a limiting factor in sorption reactions involving hydrous iron and manganese oxides.

Because of diagenetic cycling, Ennis Lake sediments should be elevated in arsenic, manganese, and iron (0 - 10 cm interval) when compared to the concentrations of the Madison River above Ennis Lake. Figures 23A, 23B, and 24A suggest that arsenic, manganese, and iron sediment concentrations of Ennis Lake and the Madison River above Ennis Lake represent two separate populations. However, the sediment arsenic concentrations of Ennis Lake are highly variable and completely overlap the range in concentrations observed on the Madison River (Figure 24A). This relatively large range in Ennis Lake concentrations is primarily controlled by the concentration at site 1B which is significantly higher (0 - 10 cm interval) when compared to the other sites (Figure 24B). It is likely that these data reflect a mixture of sediment both enriched and depleted in arsenic in the upper 10 cm. Therefore, using mean arsenic values recorded above Ennis Lake and the 0 - 10 cm interval from Ennis Lake, the sediment of the Madison River is possibly enriched by approximately 75% in Ennis Lake.

### Ennis Lake Water

The water column arsenic concentrations are highly variable throughout the lake ranging from 0.045 to 0.090 (Figure 25). In general, the sites located on the west and east sides of the lake have lower concentrations than those located near the mouth of the Madison River and in, or near, Bear Trap Canyon located at the Northeast end of the lake (Figures 25 and 26). This observed variability most likely results from multiple low-arsenic water inputs to the west and east ends (Figure 27).

The dissolved arsenic concentrations of Ennis Lake and two Madison River sites, located above and below Ennis Lake (sites AER and BER, respectively), are presented in figure 28 (relative location: Figure 27). The arsenic concentrations demonstrate the greatest variability in Ennis Lake with a range in values encompassing those observed at both Madison River sites. Furthermore, the majority of the Ennis Lake concentrations are within the range of values observed at site AER.

The Madison River receives relatively significant inputs from O'Dell and Jack Creeks (103 and 60 cfs, respectively, as reported by the USGS on 5/10/91) which are located between site AER and Ennis Lake (Figure 27). The percent dilution of Madison River arsenic concentrations by these tributaries cannot be determined directly by this study because these locations were not sampled. However, it is assumed that both O'Dell and Jack Creeks are relatively low in dissolved arsenic. This is suggested from water data collected December 12-16, 1989, which shows that the sites located on the Madison River below the

confluence of O'Dell and Jack Creeks to be lower in dissolved arsenic than those sites located just above them (Figure 4; between river km 150 and Ennis Lake). Therefore, it is unlikely that these two tributaries contribute to the high-end arsenic values in Ennis Lake.

Ennis Lake is set in a relatively broad valley which results in its large areal coverage (approximately 17 square km) and shallow depth (main body depth ranges from 1 - 4 meters, Bear Trap Canyon depth is 8 - 9 meters). Wave activity is usually substantial, therefore, it is reasonable to assume that the upper few centimeters of sediment are being periodically mixed with the overlying mildly alkaline water (pH ranged from 8.0 - 8.9). Although porewater pH commonly increases with height in the sediment column, the pH of the porewater over the zone of Mn(II) and Fe(II) precipitation is most likely lower than that of the overlying water. Relatively small increases in pH have been shown to be conducive to desorption of arsenic from iron oxyhydroxides (Fuller and Davis, 1990). Therefore, periodic mixing of the sediment with the overlying water may result in arsenic desorption thereby increasing the dissolved arsenic concentrations. Alternatively, sediment-bound arsenic may be mobilized over the winter months as Ennis Lake becomes ice-bound. The shift from aerobic to subaerobic/anoxic conditions in the water column would likely result in the reduction of Mn(IV) and Fe(III)-oxides and the release of As(V), sorbed/coprecipitated with those oxides.

All of this is difficult to substantiate without seasonal porewater and tributary data and is presented here only as possible mechanisms by which arsenic is mobilized to the water column and as possible explanations for the elevated

dissolved arsenic concentrations in Madison River lakes.

## Conclusions

The trend in dissolved arsenic indicates that the primary source of arsenic in the Madison-Missouri River system is in the headwaters of the Madison River. Multiple inputs from streams dilute the arsenic rich water of the Madison River. This is indicated by the overall appearance of the dissolved arsenic trend and supported by the relatively strong correlation with dissolved sodium. This relationship between solute arsenic and sodium indicates that arsenic is behaving conservatively and, given the filter data which suggests that solute arsenic is truly dissolved, supports a dissolved phase for arsenic transport. The lack of any correlation between dissolved arsenic and iron, aluminum, and manganese indicates little control by colloids ( $<0.45$  micron) of these metals.

The relationships between sediment-bound As and Fe, Al, and Mn suggests little control by oxyhydroxides of these metals. This is due most likely to the relatively high pH measured throughout the drainage which has been shown to be suboptimal for sorption reactions involving these constituents. The relationship between As and Fe, however, strengthens when limited to the Madison River. Given the large body of research which clearly describes arsenic's affinity for iron oxyhydroxides and the relatively constant Fe/As molar ratios, there may be some control of particulate arsenic by Fe oxyhydroxides in bed-sediment of the Madison River.

The relatively large decrease in sediment arsenic concentrations from the



Madison to the Missouri River is due primarily to mixing with the arsenic deficient sediment of the Jefferson and Gallatin Rivers. This is supported by the mixing model results which indicate that the sediment of the Madison River is diluted by approximately 60% after its confluence with these two rivers.

The research conducted on the sediment and water of Ennis Lake suggests that the sediments are acting as both a sink and a source of dissolved arsenic. The strong relationship between arsenic and manganese, and to an extent iron, suggests that diagenetic cycling is the process by which arsenic is concentrated in the sediment. This is supported by the surficial sediment concentration maxima of arsenic and manganese as well as the iron maxima which lies at a somewhat deeper depth. The periodic mixing of arsenic rich sediments with the overlying mildly alkaline water may be acting to release arsenic to the water column. As well, if anaerobic conditions prevail during the winter months then arsenic may be further mobilized as Mn(IV) and Fe(III) are reduced. All of this may possibly explain the elevated dissolved arsenic concentrations observed in all Madison River lakes.

The data collected for this study indicates that iron, aluminum, and manganese oxides, and organic carbon, play a relatively minor role in controlling dissolved arsenic concentrations. Furthermore, the dissolved arsenic concentrations are primarily controlled by dilution after its introduction into the headwaters of the Madison River. The arsenic concentrations of the Missouri River are strongly influenced by the Jefferson and Gallatin Rivers which act to further dilute the sediment and dissolved arsenic concentrations of the Madison River.

Table 1. Concentrations and (standard deviations) for U.S. Geological Survey (USGS) water standards. Values listed in mg/l. BD = Below Detection, L.O.D. = Limit of Detection.

Metal	L.O.D.	USGS T103		USGS T97	
		Given	Obtained (n=11)	Given	Obtained (n=15)
Al	0.03	0.127 (0.038)	0.112 (0.03)	0.126 (0.042)	0.112 (0.03)
As	0.05	0.003 (0.001)	BD	0.01 (0.001)	BD
Fe	0.005	0.041 (0.008)	0.037 (0.004)	0.1 (0.009)	0.098 (0.006)
Ca	0.004	54.7 (2.0)	49.5 (15.7)	54 (2.1)	53.7 (3.6)
Mn	0.002	0.009 (0.002)	0.008 (0.0003)	0.03 (0.003)	0.03 (0.002)
Na	0.02	107 (5.0)	110 (3.74)	59 (3.1)	61.4 (3.6)

Table 2. Concentrations and (standard deviations) of U.S. Geological Survey (USGS) water standards T103 and T97 after standard arsenic additions. Concentrations in mg/l.

Sample	Calculated with Standard Addition	Measured with Standard Addition	Percent Recovered
USGS T103 (n=8)	1.00	1.01 (0.004)	101 (0.029)
USGS T97 (n=7)	0.41	0.37 (0.067)	96 (0.066)

Table 3. Concentrations and (standard deviations) for HCl-extracts of National Bureau of Standards (NBS) and U.S. Geological Survey (USGS) sediment standards. Values listed in mg/kg. Because the standards are certified for total metals only, this data is restricted to precision evaluation.

Metal	USGS SED2 (n=57)	NBS 1646 (n=30)	NBS 2704 (n=29)
Al	3152 (186)	4208 (311)	3033 (318)
As	112 (4.3)	4.1 (2.2)	11.3 (6.2)
Ca	16211 (250)	3263 (50.4)	23622 (678)
Fe	8718 (342)	7865 (497)	10075 (621)
Mn	1375 (22.8)	101 (6.6)	340 (8.8)
Na	39.6 (4.9)	10387 (992)	26.1 (4.0)

Table 4. Results of 10 mg/l standard arsenic additions to composite sediment sample extracts chosen at random.

Volume Added (μl)	Sample Volume (ml)	Sample	Pre-Spike Measurement (mg/l)	Calculated with Spike (mg/l)	Measured with Spike (mg/l)	Percent Recovered
140	5	JE Comp.	0.082	0.352	0.362	103
70	5	JE Comp.	0.082	0.219	0.228	104
60	5	MO Comp.	0.264	0.379	0.372	98
20	5	MO Comp.	0.264	0.303	0.299	99
70	5	MA Comp.	0.737	0.865	0.868	100
140	5	MA Comp.	0.737	0.989	0.989	100
140	5	MA Comp.	0.631	0.886	0.878	99
70	5	MA Comp.	0.631	0.76	0.746	98
40	5	MA Comp.	0.631	0.705	0.704	100
80	5	EN Comp.	0.55	0.699	0.694	99
40	5	EN Comp.	0.55	0.625	0.614	98
140	5	HL Comp.	1.4	1.63	1.64	101
70	5	HL Comp.	1.4	1.52	1.52	100
140	5	MA Comp.	1.11	1.35	1.34	99
70	5	MA Comp.	1.11	1.23	1.22	99
40	5	MA Comp.	1.11	1.18	1.17	99
80	5	JE Comp.	0.123	0.279	0.278	100
40	5	JE Comp.	0.123	0.201	0.193	96
20	5	JE Comp.	0.123	0.162	0.135	83
80	5	EN Comp.	0.59	0.738	0.73	99
40	5	EN Comp.	0.59	0.665	0.664	100
20	5	EN Comp.	0.59	0.627	0.615	98
60	5	MO Comp.	0.284	0.399	0.363	91
40	5	MO Comp.	0.284	0.361	0.339	94
20	5	MO Comp.	0.284	0.323	0.297	92
140	5	JE Comp.	0.115	0.384	0.306	80
70	5	JE Comp.	0.115	0.251	0.219	87

Table 4 continued.

Volume Added (μl)	Sample Volume (ml)	Sample	Pre-Spike Measurement (mg/l)	Calculated with Spike (mg/l)	Measured with Spike (mg/l)	Percent Recovered
20	10	MO6	0.017	0.0369	0.036	98
40	10	MO6	0.017	0.0568	0.0555	98
20	10	MO2	0.0204	0.0403	0.0348	86
40	10	MO2	0.0204	0.0601	0.0562	93
150	10	MA15B; 3	0.215	0.36	0.367	102
200	10	MA15B; 3	0.215	0.407	0.434	107
150	10	MA14B; 1	0.379	0.521	0.507	97
200	10	MA14B; 1	0.379	0.568	0.541	95
150	10	MA16B; 2	0.209	0.354	0.373	105
200	10	MA16B; 2	0.209	0.401	0.4	100
150	10	MA13B; 1	0.232	0.376	0.355	94
200	10	MA13B; 1	0.232	0.423	0.377	89
150	10	MA14B; 3	0.353	0.495	0.499	101
200	10	MA14B; 3	0.353	0.542	0.535	99
20	10	EN102	0.0333	0.0532	0.0444	83
40	10	EN102	0.0333	0.073	0.0608	83
20	10	BER0500	0.03	0.0499	0.0499	100
40	10	BER0500	0.03	0.0697	0.0686	98
20	10	EN114	0.0318	0.0517	0.0421	81
40	10	EN114	0.0318	0.0715	0.0524	73
20	4	JE4-1	0.12	0.169	0.16	95
20	3.5	JE4-2	0.133	0.189	0.157	83
20	4	JE4-3	0.127	0.176	0.155	88
50	3.5	MA5-1	0.55	0.683	0.679	99
50	3	MA5-2	0.544	0.699	0.662	95
50	4	MA5-3	0.56	0.677	0.622	92

Table 4 continued.

Volume Added ( $\mu$ l)	Sample Volume (ml)	Sample	Pre-Spike Measurement (mg/l)	Calculated with Spike (mg/l)	Measured with Spike (mg/l)	Percent Recovered
150	10	EN1B; 3-4	0.373	0.515	0.515	100
200	10	EN1B; 3-4	0.373	0.561	0.543	97
150	10	EN8B; 0-1	0.394	0.536	0.535	100
200	10	EN8B; 0-1	0.394	0.582	0.596	102
150	10	EN1B; 1-2	0.38	0.522	0.519	99
200	10	EN1B; 1-2	0.38	0.569	0.576	101
150	10	EN9B; 3-4	0.375	0.517	0.514	99
200	10	EN9B; 3-4	0.375	0.564	0.562	100
150	10	EN9B; 4-5	0.399	0.541	0.53	98
200	10	EN9B; 4-5	0.399	0.587	0.591	101
20	10	EN111	0.083	0.103	0.097	94
40	10	EN111	0.083	0.122	0.12	98
20	10	BER1530	0.071	0.091	0.098	108
40	10	BER1530	0.071	0.111	0.112	101
20	10	AERO600	0.076	0.096	0.087	91
40	10	AERO600	0.076	0.116	0.113	97
20	10	EN74	0.065	0.085	0.075	88
40	10	EN74	0.065	0.105	0.101	96
150	10	EN3B; 1-2	0.395	0.537	0.519	97
200	10	EN3B; 1-2	0.395	0.583	0.58	99
150	10	EN6B; 0-1	0.426	0.567	0.558	98
200	10	EN6B; 0-1	0.426	0.614	0.591	96
150	10	EN4B; 20-21	0.246	0.39	0.368	94
200	10	EN4B; 20-21	0.246	0.437	0.415	95
20	10	MO4	0.0215	0.0414	0.0389	94
40	10	MO4	0.0215	0.0612	0.0559	91

Table 4 continued.

Volume Added ( $\mu$ l)	Sample Volume (ml)	Sample	Pre-Spike Measurement (mg/l)	Calculated with Spike (mg/l)	Measured with Spike (mg/l)	Percent Recovered
140	5	MA Comp.	0.703	0.956	0.891	93
70	5	MA Comp.	0.703	0.831	0.837	101
140	5	MA Comp.	0.628	0.883	0.873	99
70	5	MA Comp.	0.628	0.757	0.757	100
40	5	MA Comp.	0.628	0.702	0.684	97
80	5	EN Comp.	0.544	0.693	0.706	102
40	5	EN Comp.	0.544	0.619	0.649	105
20	5	EN Comp.	0.544	0.582	0.596	102
140	5	HL Comp.	1.39	1.62	1.62	100
70	5	HL Comp.	1.39	1.51	1.5	99
40	5	HL Comp.	1.39	1.46	1.48	101
140	5	MA Comp.	0.606	0.861	0.857	99
70	5	MA Comp.	0.606	0.717	0.73	102
80	5	JE Comp.	0.085	0.241	0.237	98
40	5	JE Comp.	0.085	0.164	0.166	101
80	5	MO Comp.	0.312	0.464	0.465	100
40	5	MO Comp.	0.312	0.389	0.387	99
20	5	JE Comp.	0.108	0.147	0.149	101
10	5	JE Comp.	0.108	0.128	0.122	95
140	5	MA Comp.	0.73	0.982	0.977	99
70	5	MA Comp.	0.73	0.858	0.852	99
60	5	MO Comp.	0.297	0.412	0.39	95
20	5	MO Comp.	0.297	0.336	0.316	94
40	5	MO Comp.	0.297	0.374	0.365	98

Table 5. Results of 100 mg/l standard calcium additions to composite sediment sample extracts chosen at random.

Volume Added (μl)	Sample Volume (ml)	Sample	Pre-Spike Measurement (mg/l)	Calculated with Spike (mg/l)	Measured with Spike (mg/l)	Percent Recovered
4	5	DGA Comp.	48.1	71.17	71.7	101
2	5	DGA Comp.	48.1	62.93	63.1	100
4	5	DTO Comp.	42.4	68	68.2	100
2	5	DTO Comp.	42.4	58.86	59.6	101
4	5	DOM Comp.	41.8	67.67	71.2	105
2	5	DOM Comp.	41.8	58.43	61.3	105
4	5	DGA Comp.	46.5	70.28	75.6	107
2	5	DGA Comp.	46.5	61.78	65.8	106
4	5	DTO Comp.	42.4	68	73.6	108
2	5	DTO Comp.	42.4	58.85	62.5	106
4	5	DJE Comp.	74	85.55	90.9	106
2	5	DJE Comp.	74	81.43	85.3	105



Table 6. Average measured value and (standard deviation) for selected elements from data set and predicted from mixing model. \*= used for mixing calculation.

Site	Ca*		Carbonate Carbon	
	Measured	Predicted	Measured	Predicted
Missouri River above Toston Reservoir	34826 (1711)	NA	10220 (601)	10111 (2324)
Jefferson and Gallatin Rivers Combined	53178 (11361)		16256 (3859)	
Madison River below Ennis Lake	9260 (1557)		1625 (634)	

Site	As		Fe	
	Measured	Predicted	Measured	Predicted
Missouri River above Toston Reservoir	13.1 (7.0)	25.3 (7.5)	6297 (836)	6165 (1633)
Jefferson and Gallatin Rivers Combined	6 (2.8)		5557 (444)	
Madison River below Ennis Lake	51.9 (18.7)		7006 (1604)	

Table 6 continued.

Site	Al		Na	
	Measured	Predicted	Measured	Predicted
Missouri River above Toston Reservoir	4193 (374)	3618 (940)	69.9 (14.1)	87 (24)
Jefferson and Gallatin Rivers Combined	3638 (710)		67.9 (10.1)	
Madison River below Ennis Lake	3589 (700)		113 (18.8)	

Site	Mn	
	Measured	Predicted
Missouri River above Toston Reservoir	395 (153)	850 (218)
Jefferson and Gallatin Rivers Combined	923 (397)	
Madison River below Ennis Lake	748 (523)	

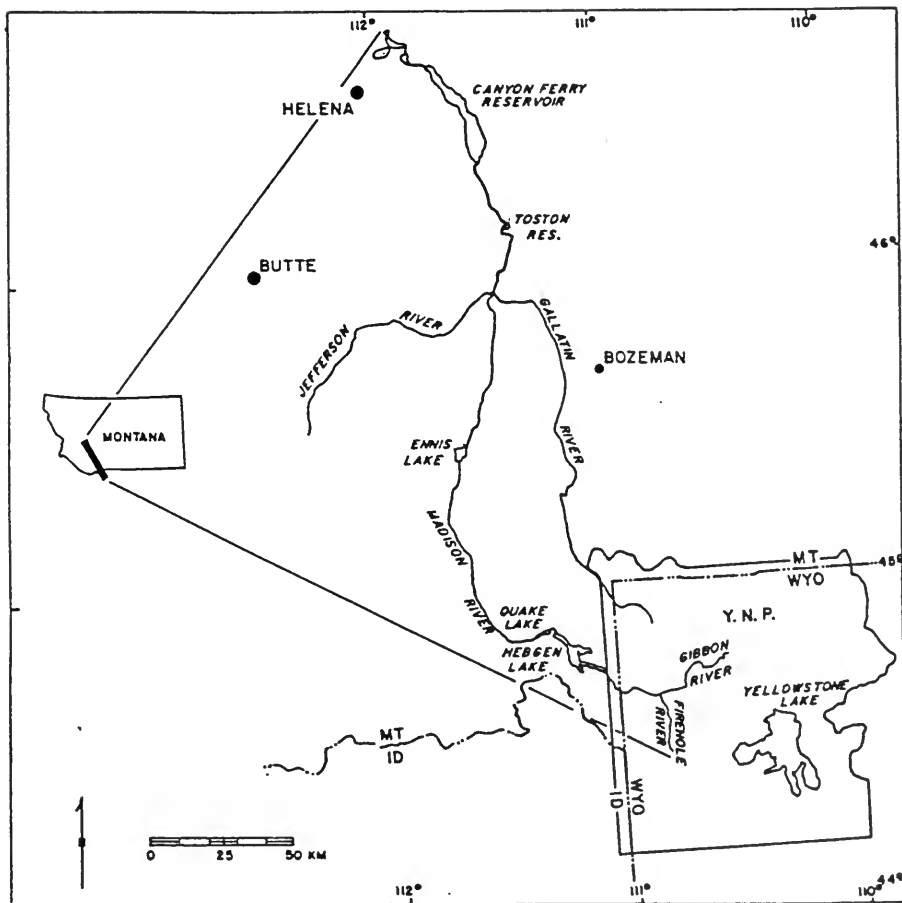
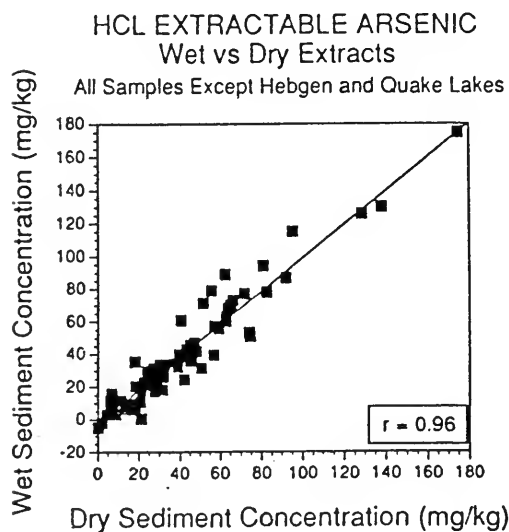
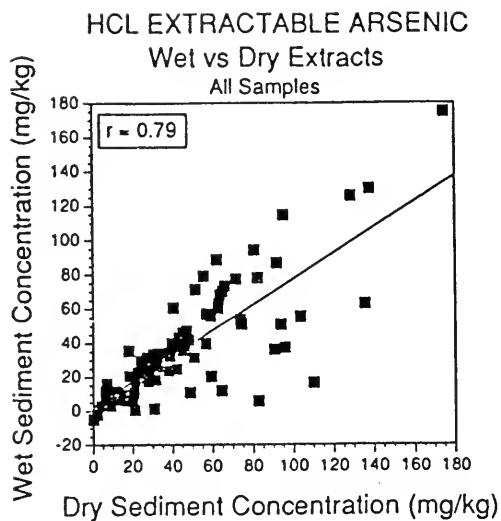


Figure 1. Map showing relative location of the study area.



Figures 2A and 2B. Comparison of wet and dry sediment arsenic concentrations for the entire data set and a data set excluding Hebgen and Quake Lakes

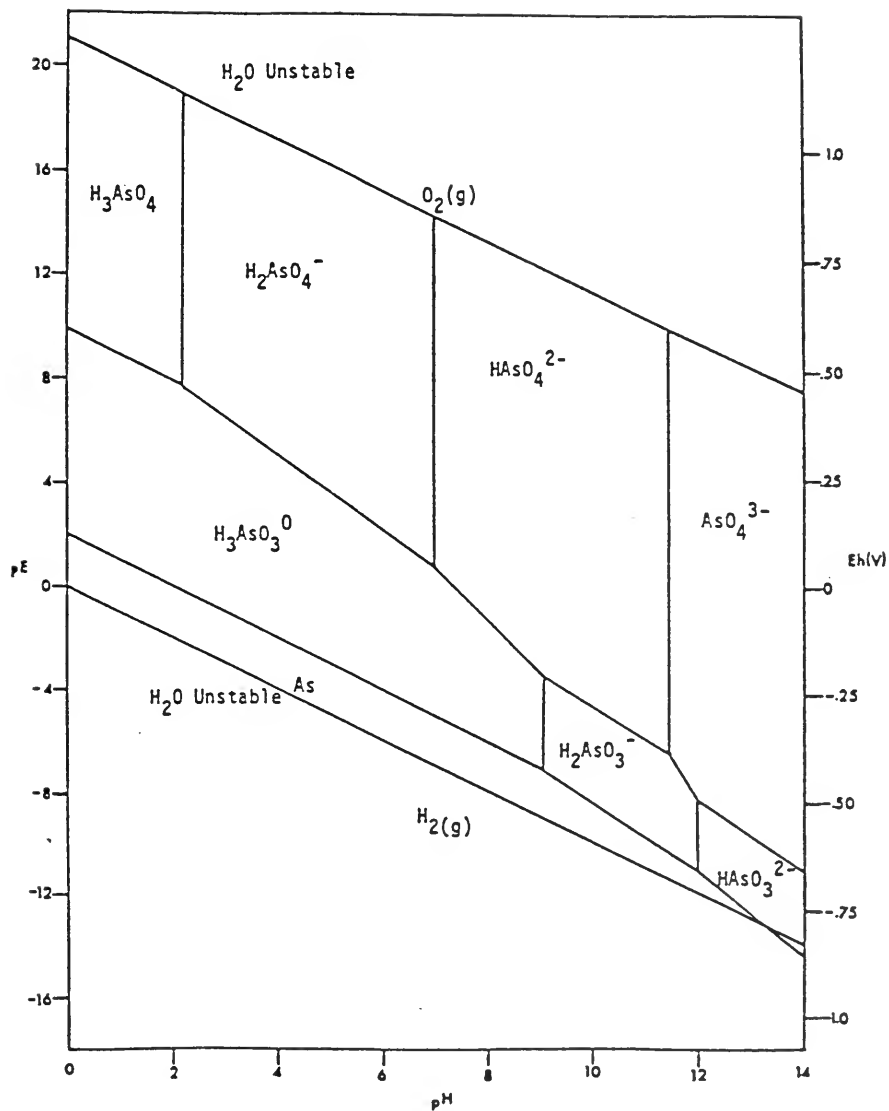


Figure 3. Eh - pH diagram for an As - H<sub>2</sub>O system at 25 °C with total arsenic species of 50 µg/L (copied from Mok and Wai, 1985).

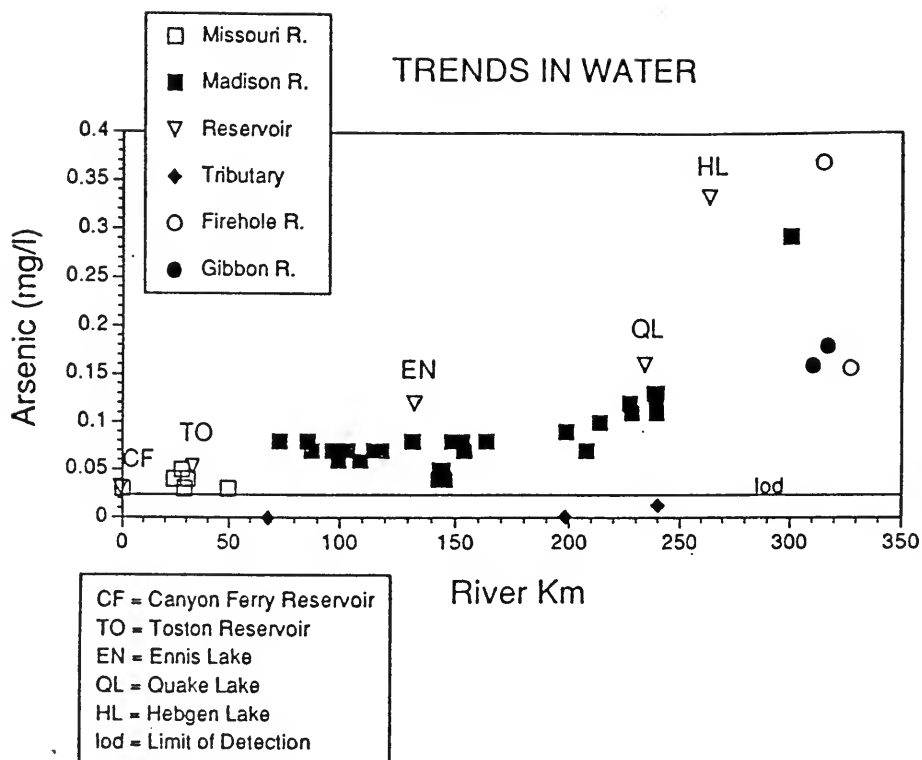
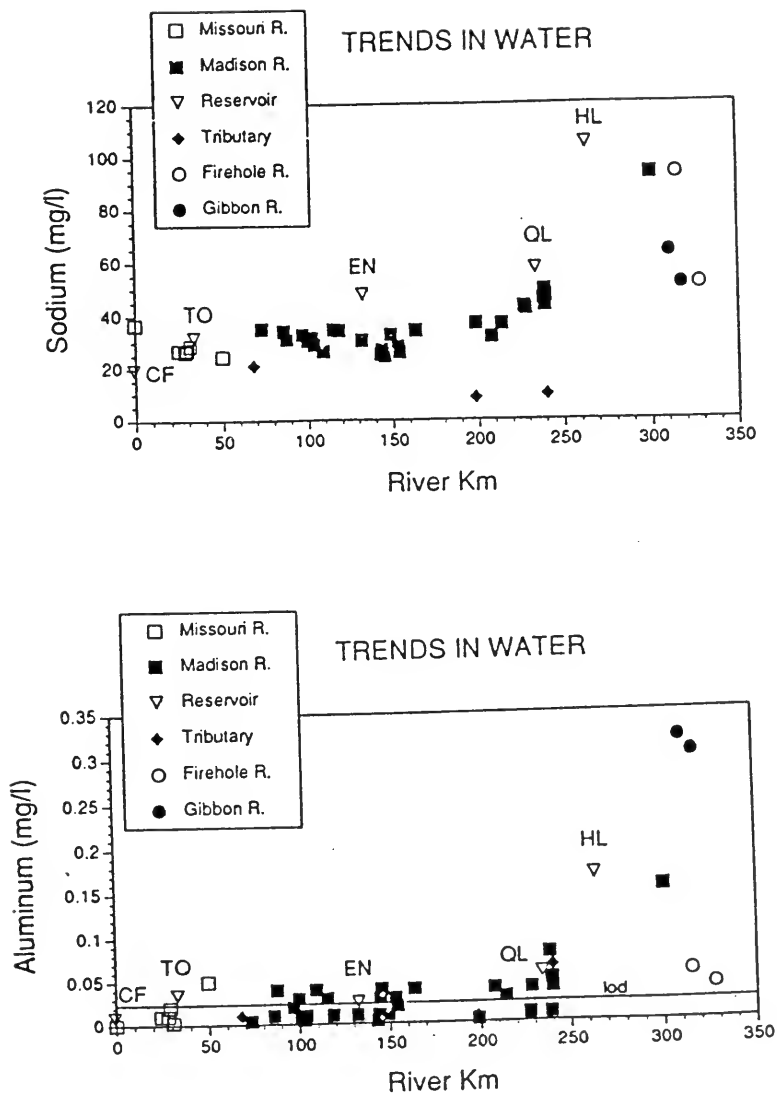
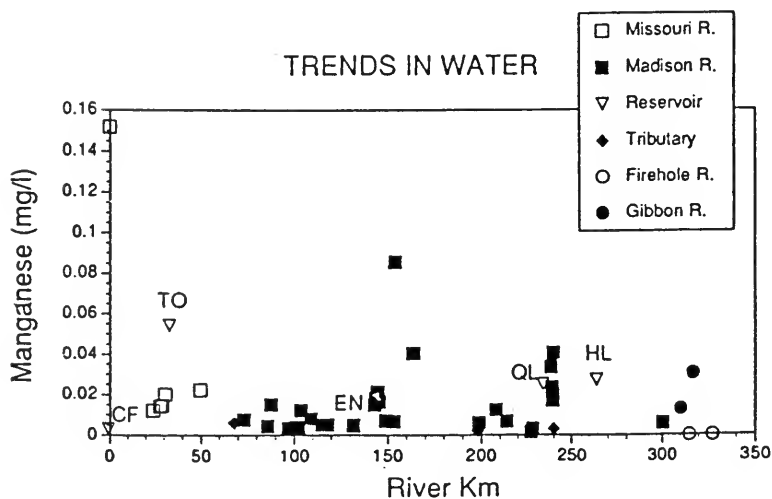
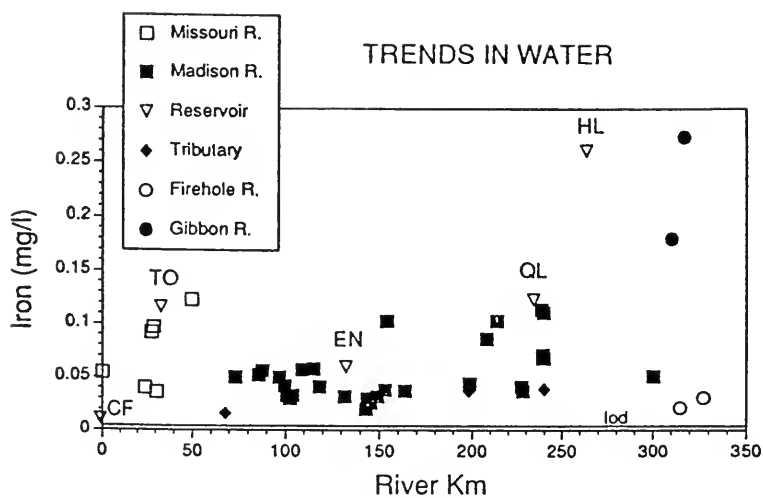


Figure 4. Dissolved arsenic concentrations with distance from the uppermost sampling locations on the Firehole and Gibbon Rivers.

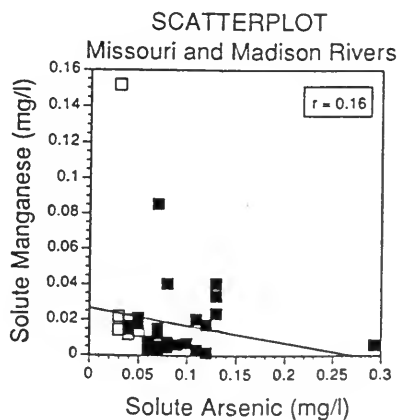
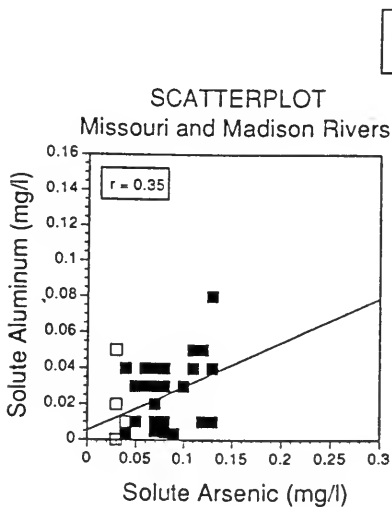
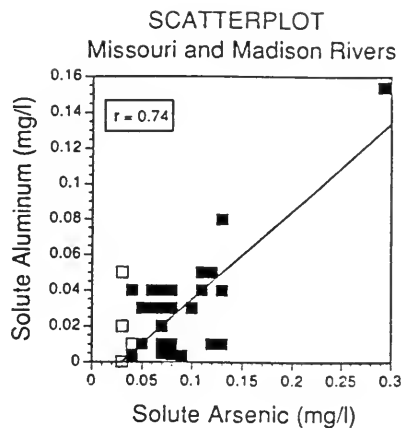
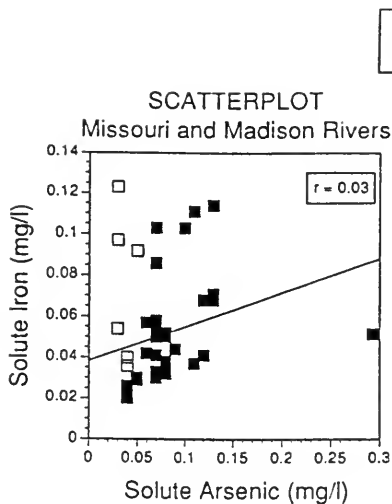


Figures 5A and 5B. Dissolved sodium and aluminum concentrations with distance from the uppermost sampling locations on the Firehole and Gibbon Rivers.



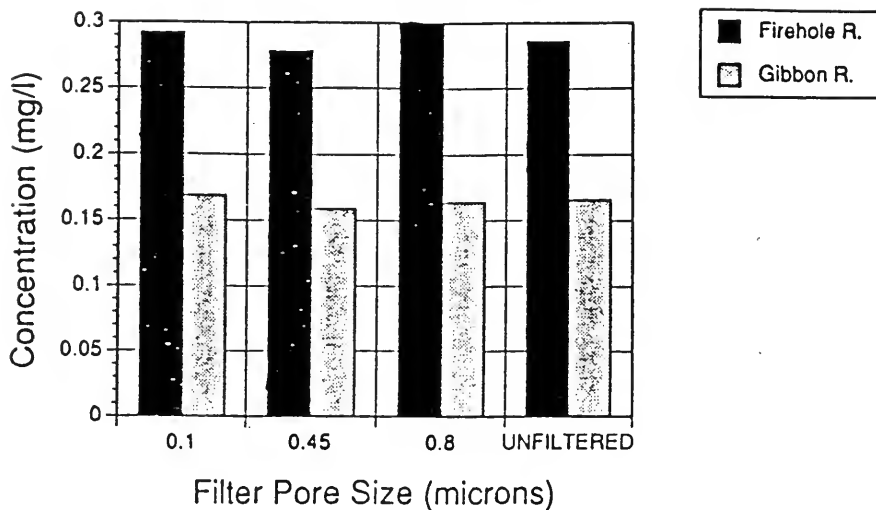
Figures 6A and 6B. Dissolved iron and manganese concentrations with distance from the uppermost sampling locations on the Firehole and Gibbon Rivers.



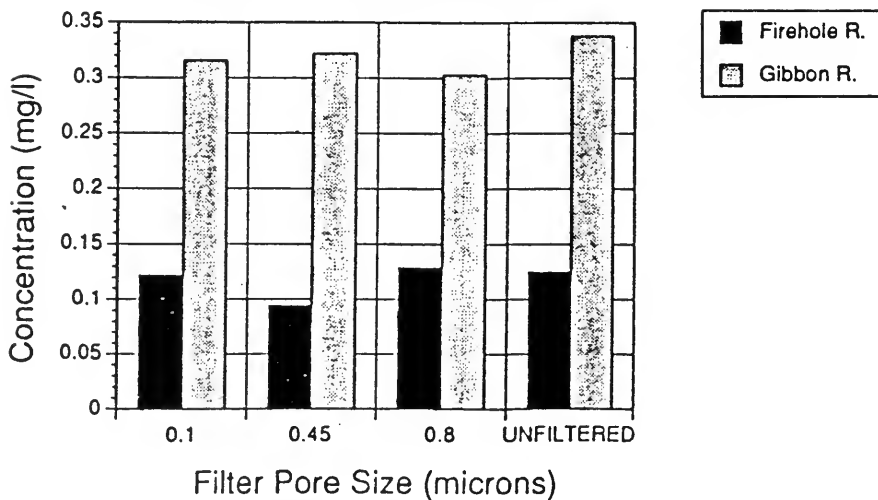


Figures 7A - 7D. Scatterplots of dissolved arsenic vs. dissolved iron, aluminum, and manganese for the Missouri and Madison Rivers only.

### WATER COLUMN ARSENIC Firehole and Gibbon Rivers

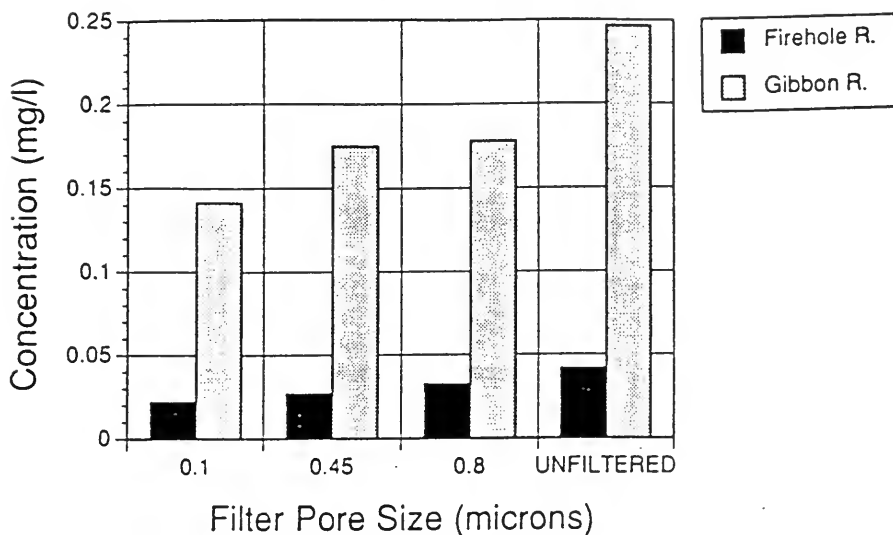


### WATER COLUMN ALUMINUM Firehole and Gibbon Rivers

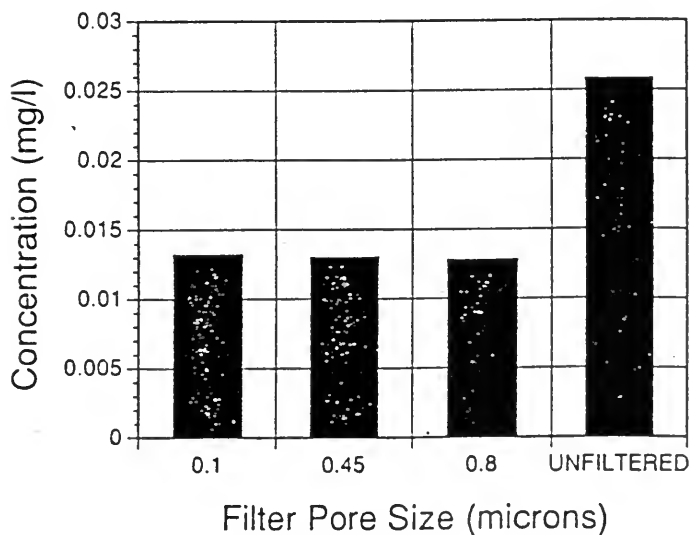


Figures 8A and 8B. Dissolved arsenic and aluminum concentrations for samples collected from the same site using various filter pore sizes.

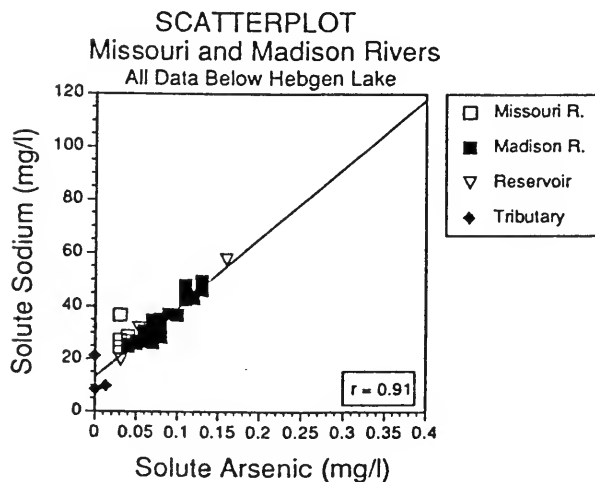
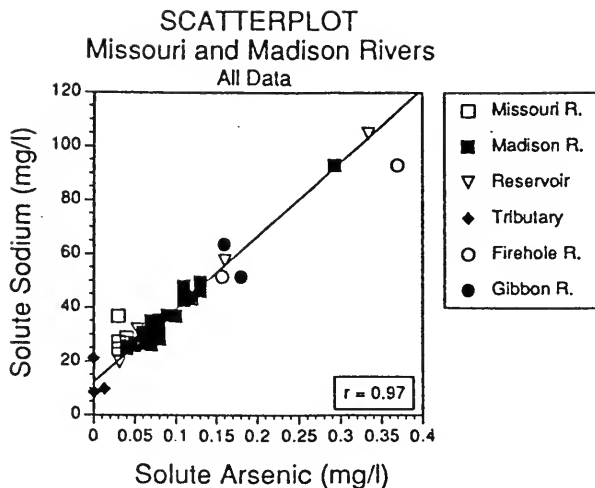
### WATER COLUMN IRON Firehole and Gibbon Rivers



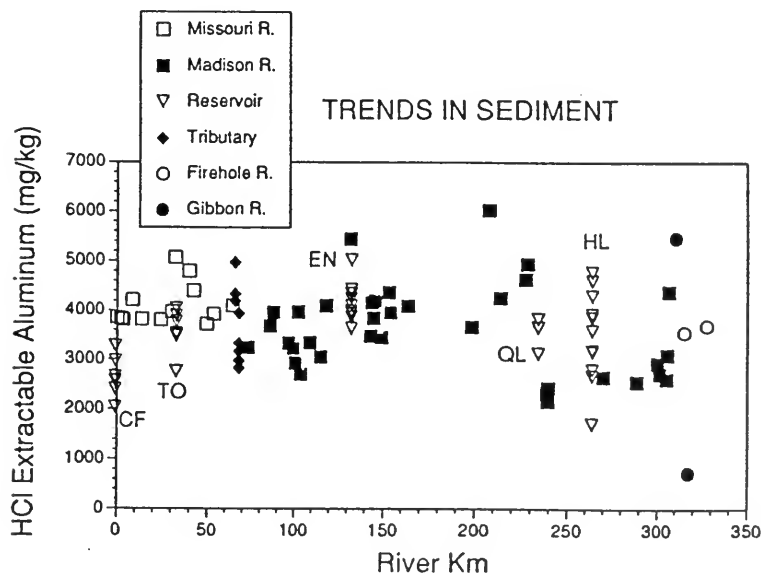
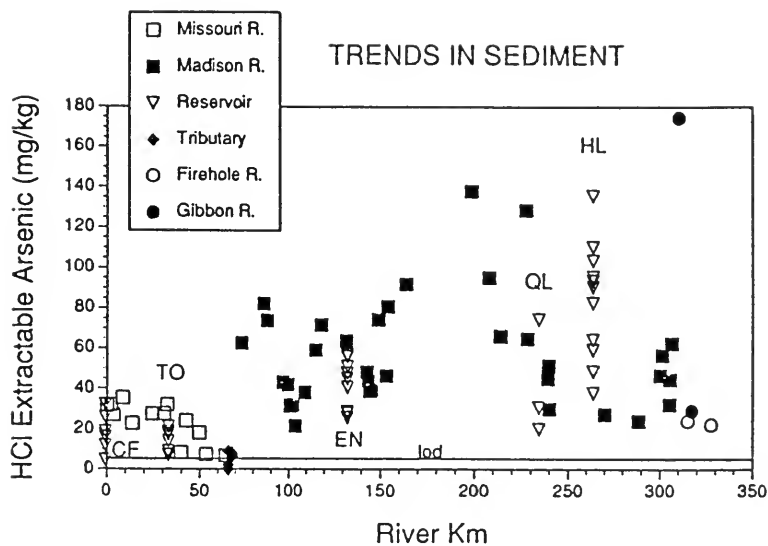
### WATER COLUMN MANGANESE Gibbon River



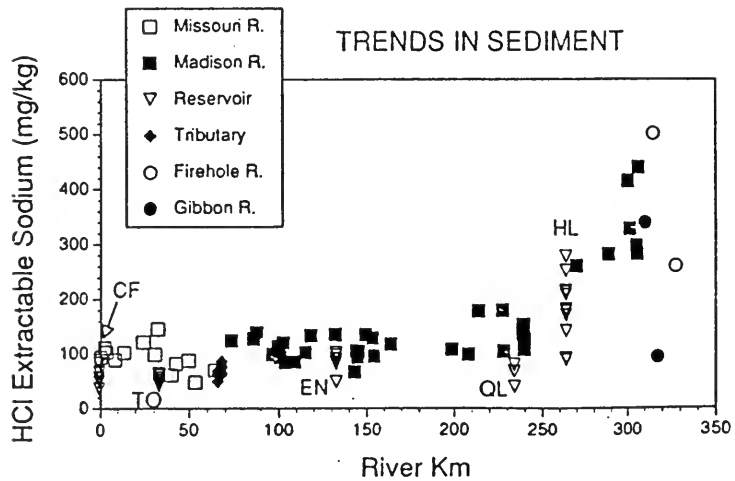
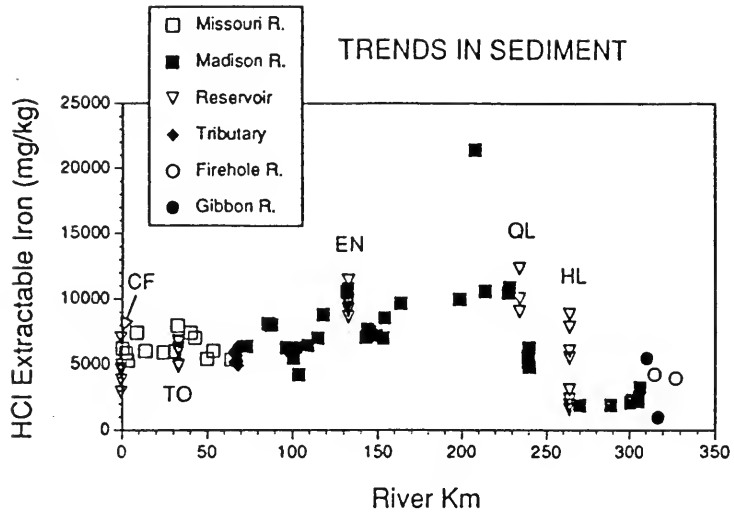
Figures 9A and 9B. Dissolved iron and manganese concentrations for samples collected from the same site using various filter pore sizes (Firehole River manganese concentrations were below the detection limit).



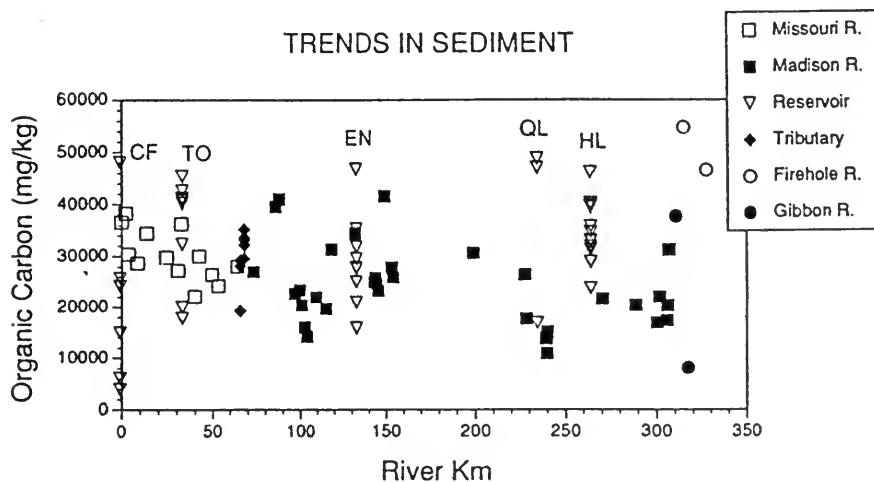
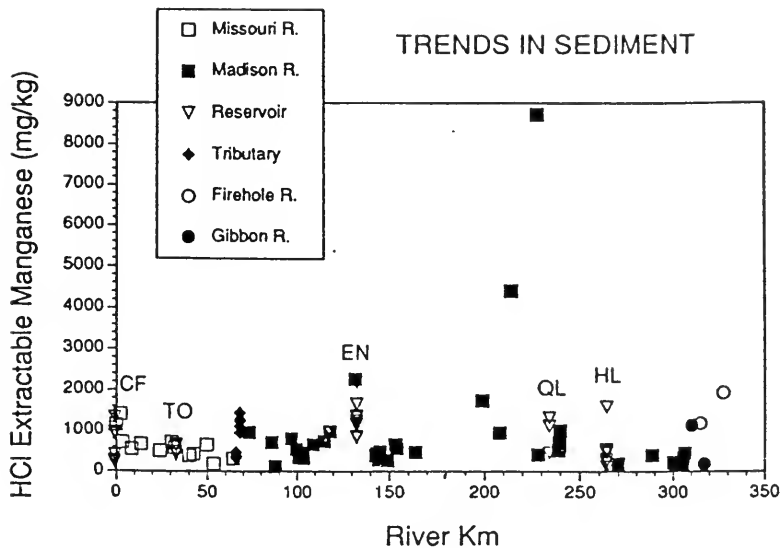
Figures 10A and 10B. Scatterplots of dissolved arsenic vs. dissolved sodium for the entire data set and all data below Hebgen Lake.



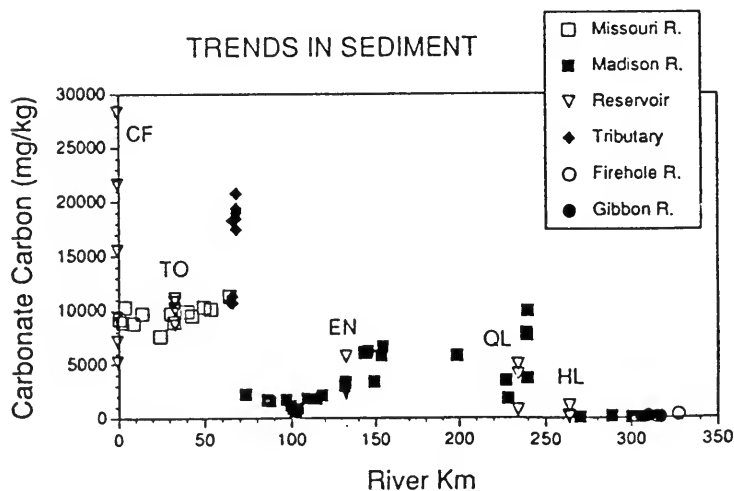
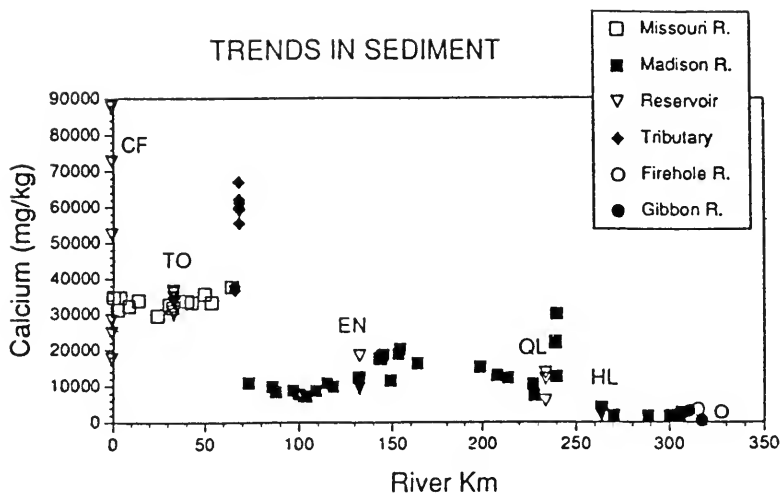
Figures 11A and 11B. HCl-extractable arsenic and aluminum concentrations with distance from the uppermost sampling locations on the Firehole and Gibbon Rivers.



Figures 12A and 12B. HCl-extractable iron and sodium concentrations with distance from the uppermost sampling locations on the Firehole and Gibbon Rivers.

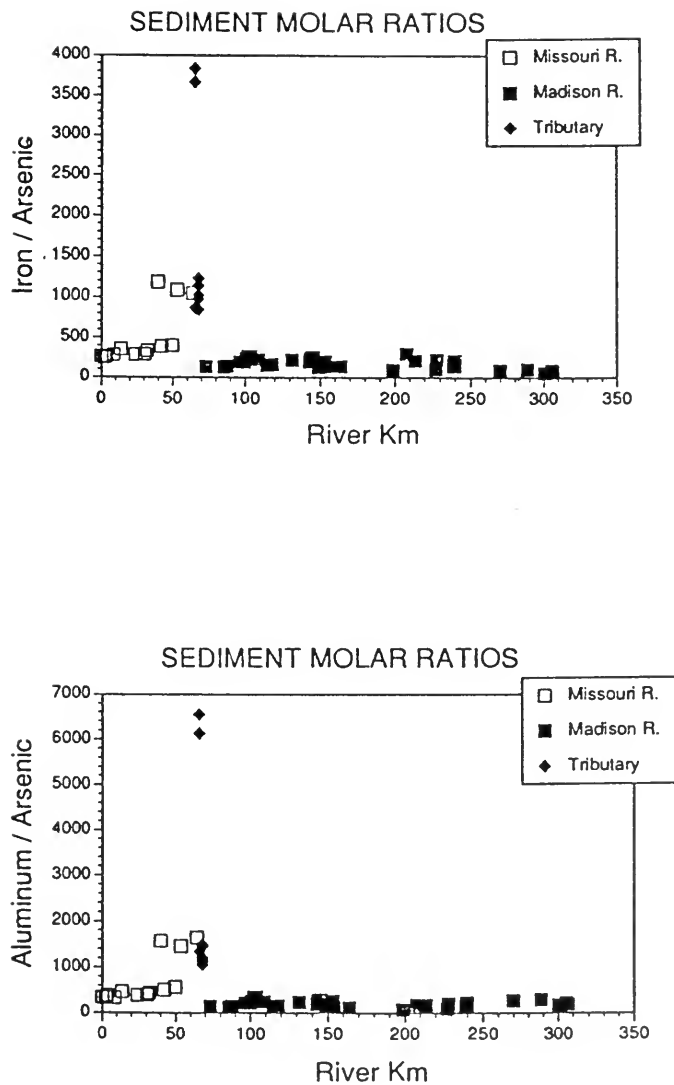


Figures 13A and 13B. HCl-extractable manganese and organic carbon concentrations with distance from the uppermost sampling locations on the Firehole and Gibbon Rivers.

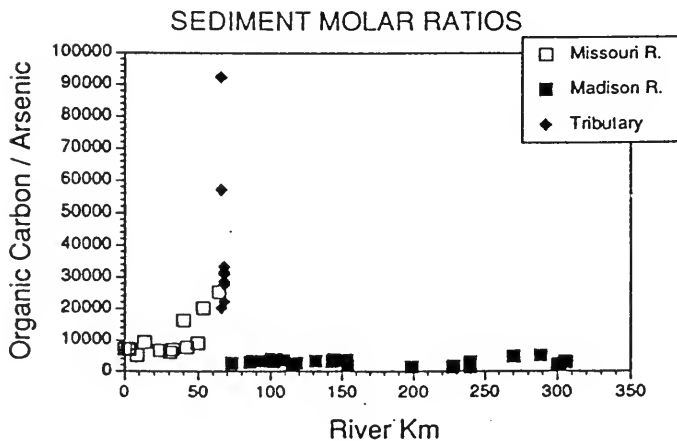
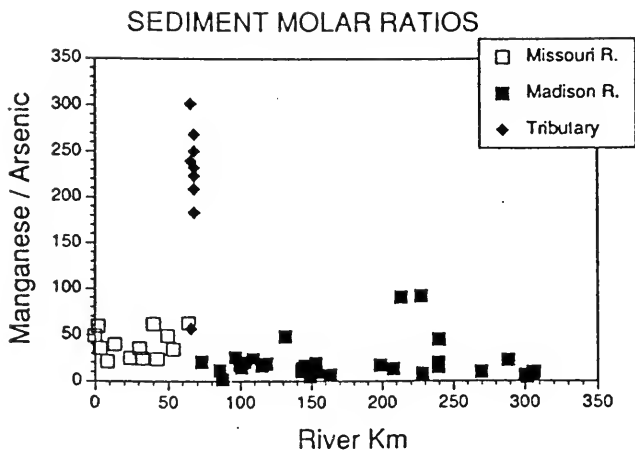


Figures 14A and 14B. HCl-extractable calcium and carbonate carbon concentrations with distance from the uppermost sampling locations on the Firehole and Gibbon Rivers.

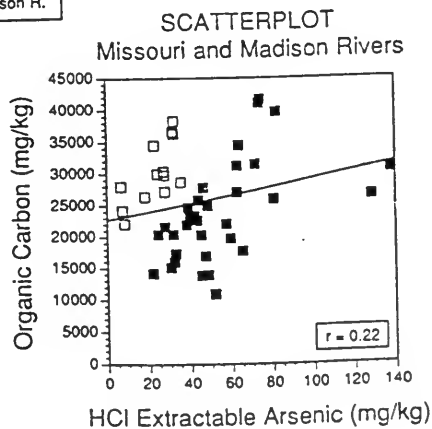
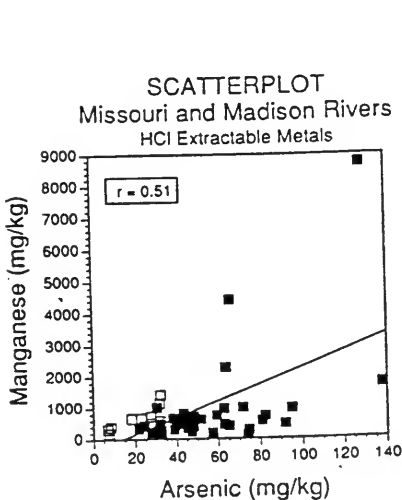
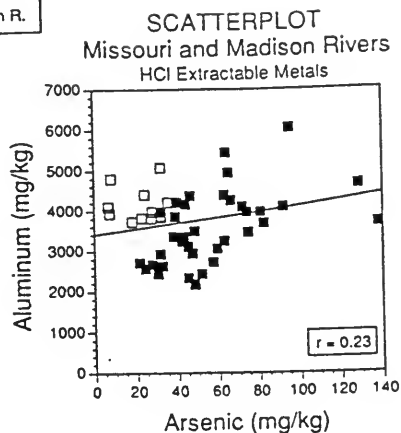
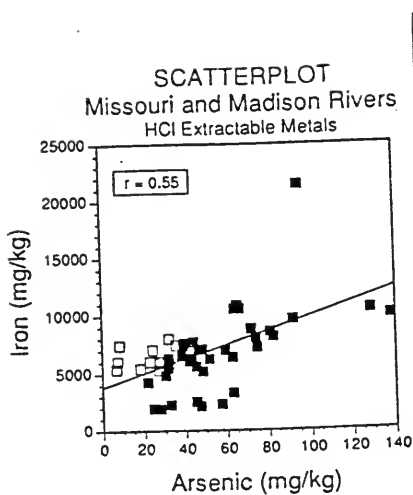




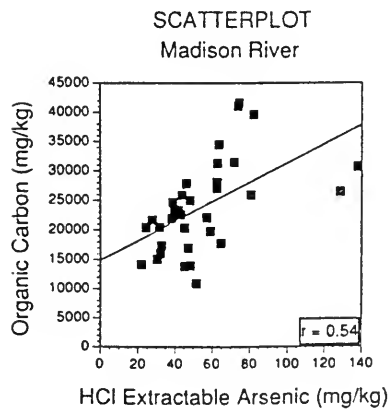
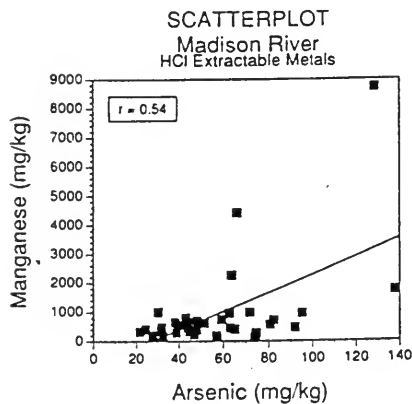
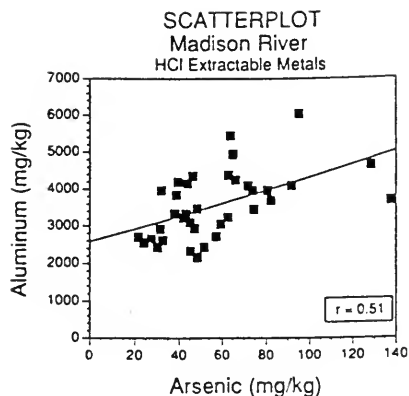
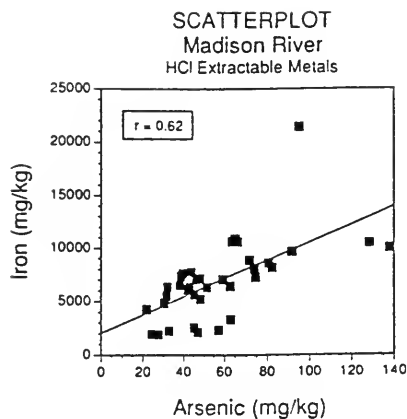
Figures 15A and 15B. HCl-extractable Fe/As and Al/As molar ratios for the Missouri, Madison, Jefferson, and Gallatin Rivers only with distance from the Madison River headwaters.



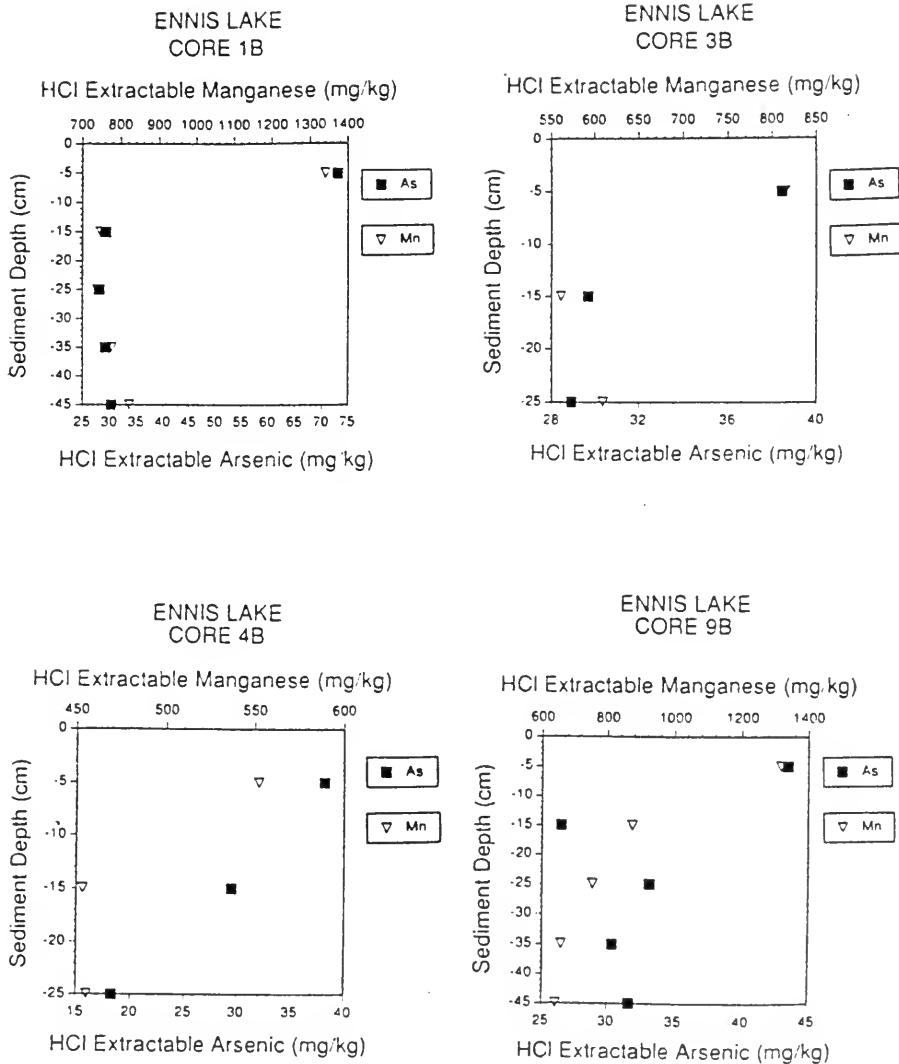
Figures 16A and 16B. HCl-extractable Mn/As and organic carbon/As molar ratios for the Missouri, Madison, Jefferson, and Gallatin Rivers only with distance from the Madison River headwaters.



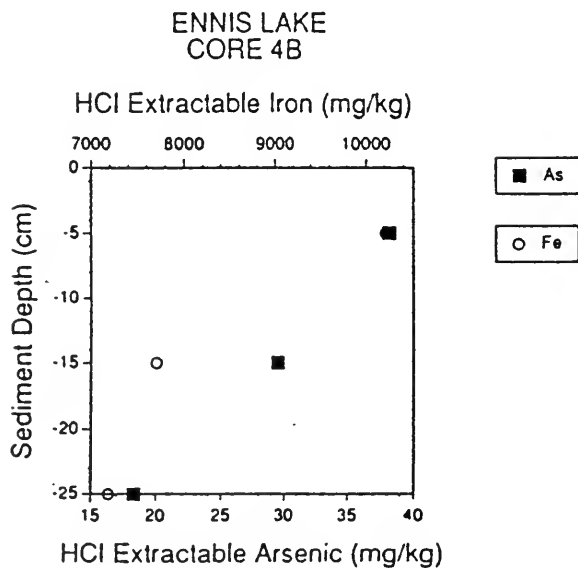
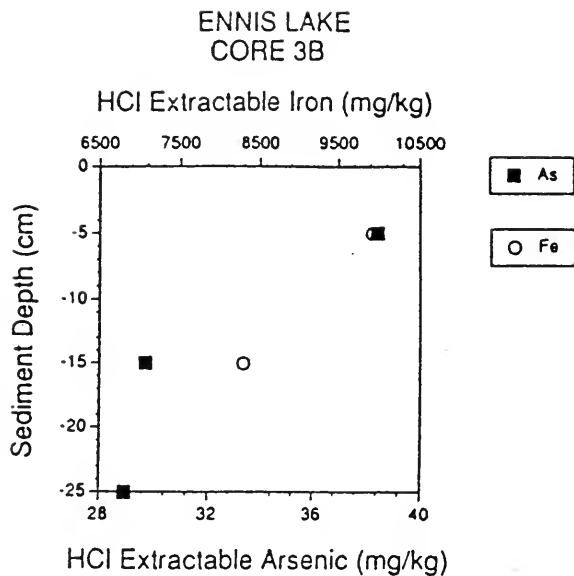
Figures 17A - 17D. Scatterplots of HCl-extractable arsenic vs. iron, aluminum, manganese, and organic carbon for the Missouri and Madison Rivers only.



Figures 18A - 18D. Scatterplots of HCl-extractable arsenic vs. iron, aluminum, manganese, and organic carbon for the Madison River only.

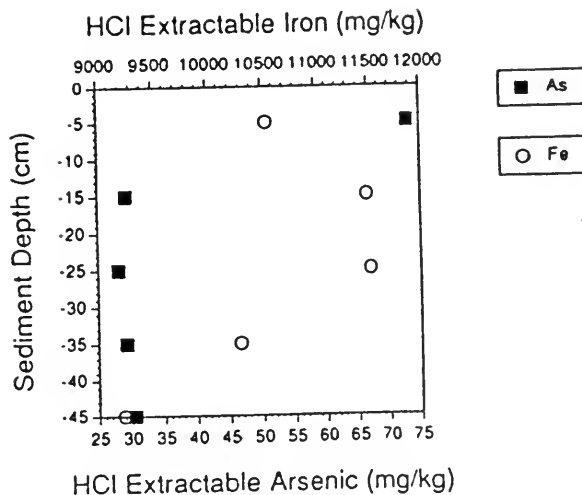


Figures 19A - 19D. Relationship between arsenic and manganese with increasing sediment depth for cores 1B, 3B, 4B, and 9B.

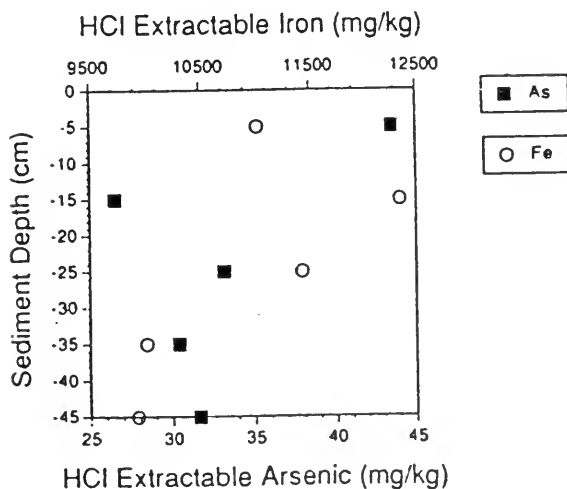


Figures 20A and 20B. Relationship between arsenic and iron with increasing sediment depth for cores 3B and 4B.

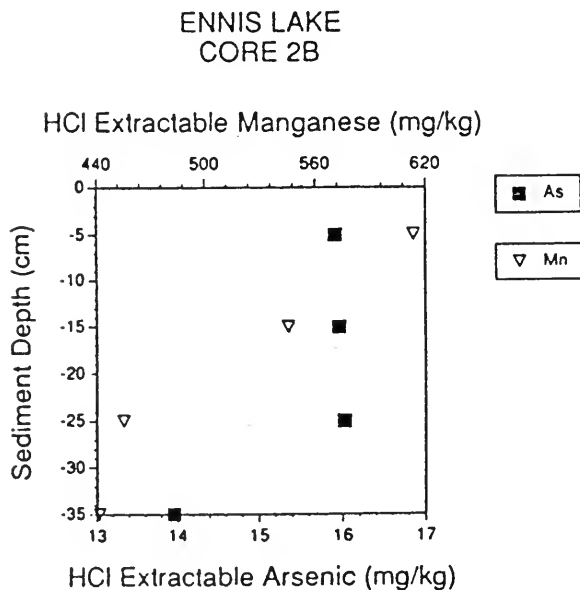
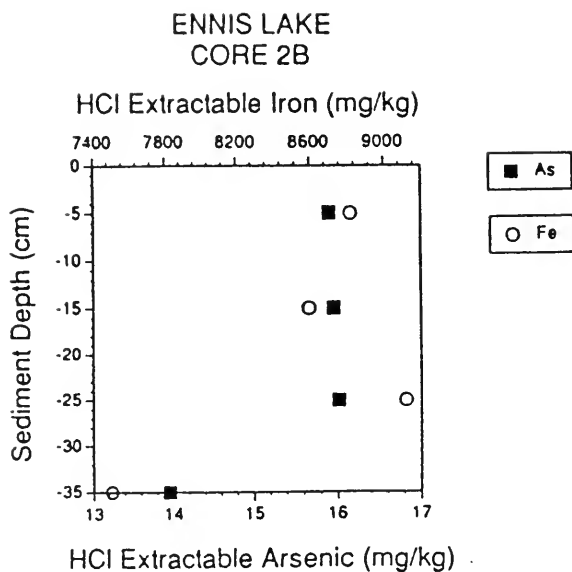
# ENNIS LAKE CORE 1B



# ENNIS LAKE CORE 9B

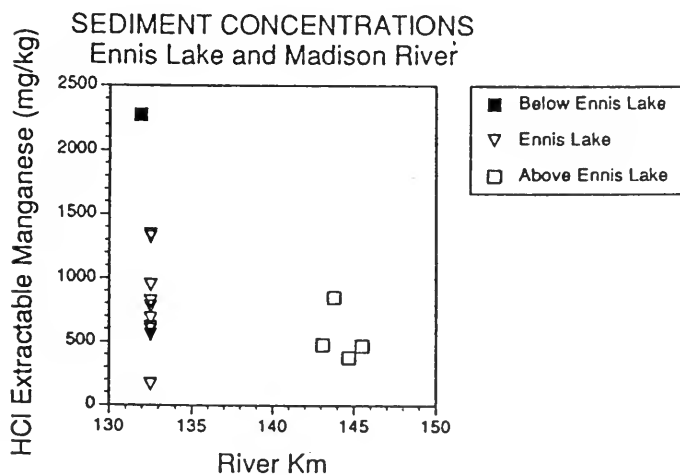
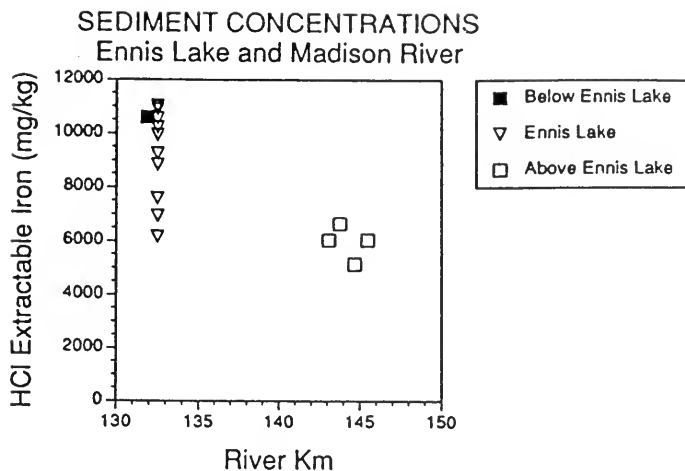


Figures 21A and 21B. Relationship between arsenic and iron with increasing sediment depth for cores 1B and 9B.



Figures 22A and 22B. Relationship between arsenic and iron and arsenic and manganese with increasing sediment depth for core 2B.





Figures 23A and 23B. Relationship between sample locations for HCl-extractable iron and manganese.

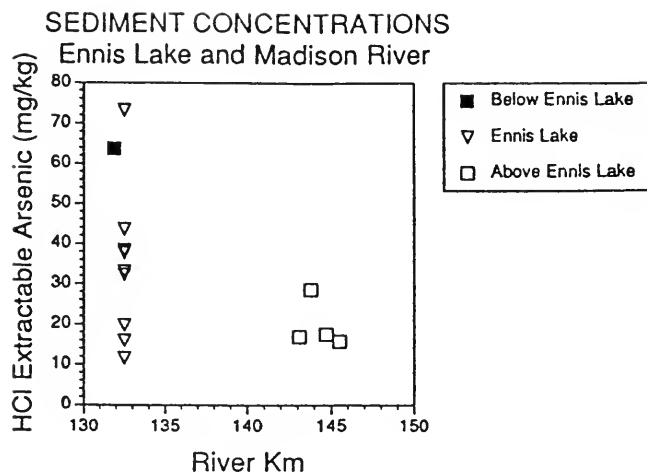


Figure 24A. Relationship between sample locations for HCl-extractable arsenic.

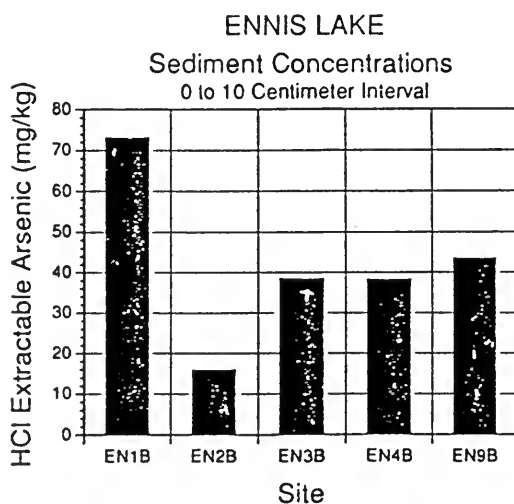


Figure 24B. Concentrations of HCl-extractable arsenic from the 0 to 10 centimeter interval with respect to sample location on Ennis Lake.

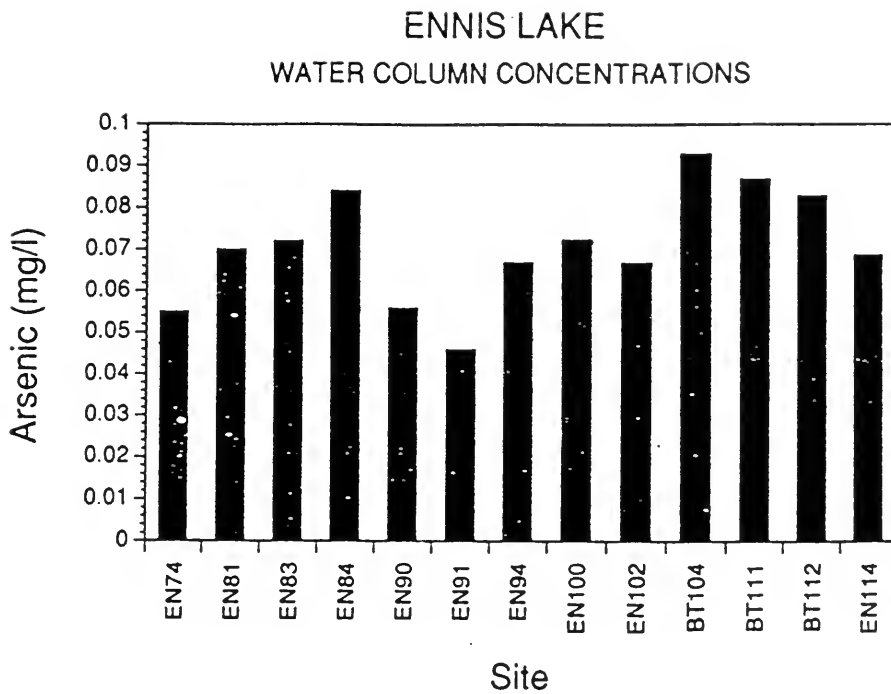


Figure 25. Concentration of dissolved arsenic in samples collected from Ennis Lake.

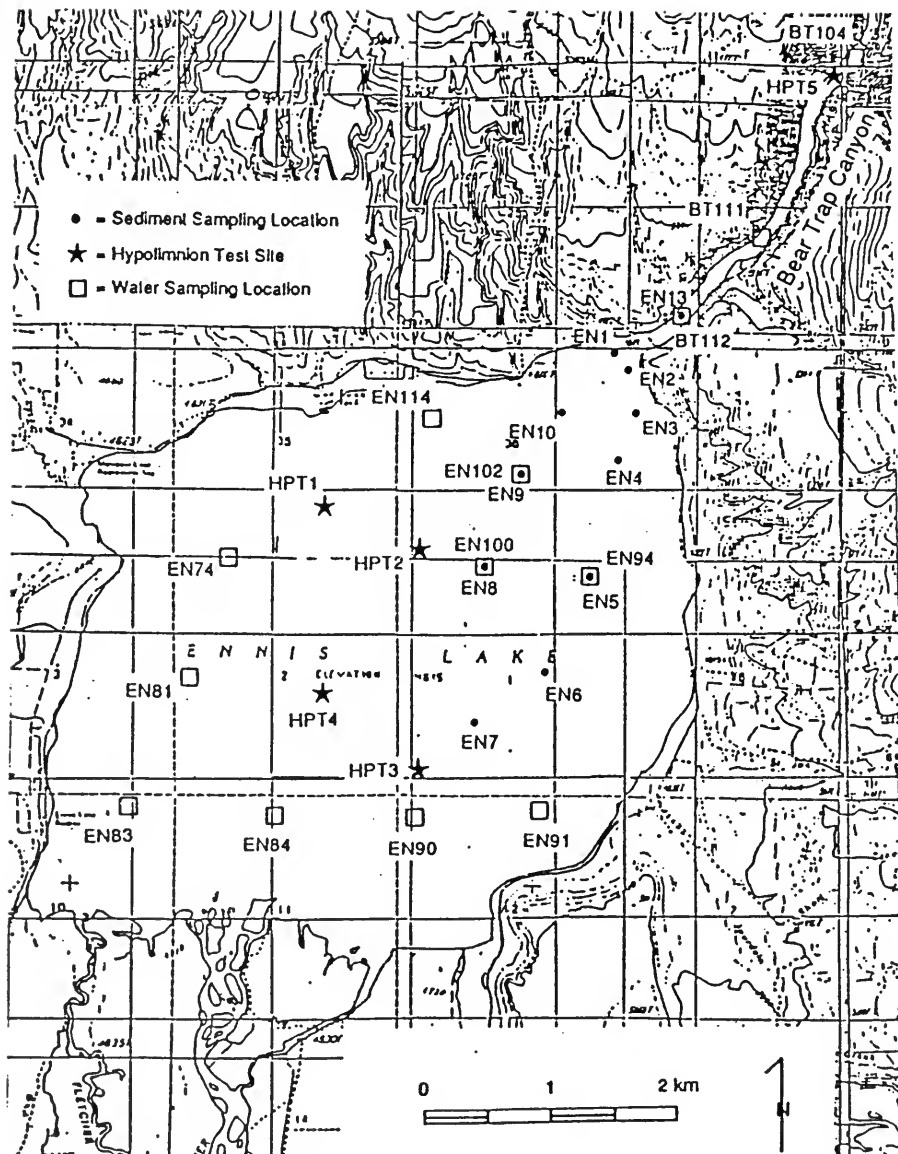


Figure 26. Map showing relative location of Ennis Lake sediment and water sampling stations and hypolimnion test sites.

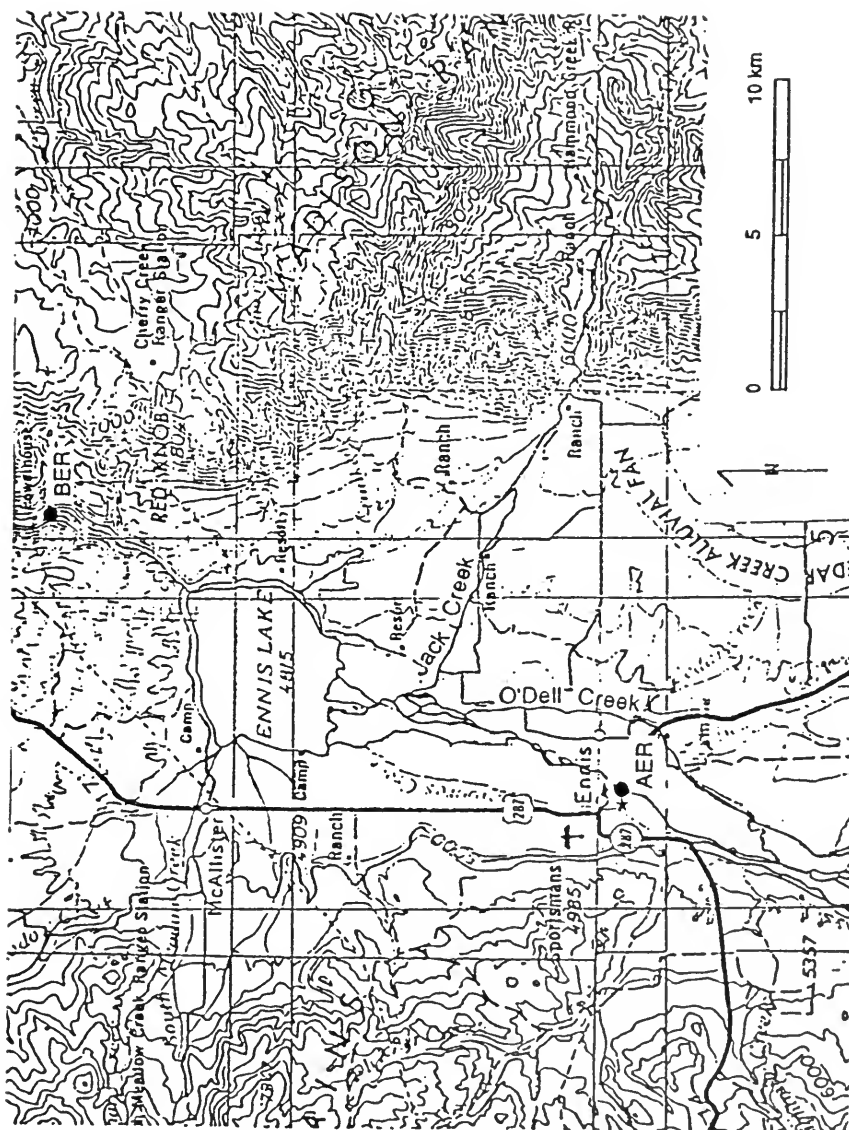


Figure 27. Map showing location of Ennis Lake and relative location of tributaries.

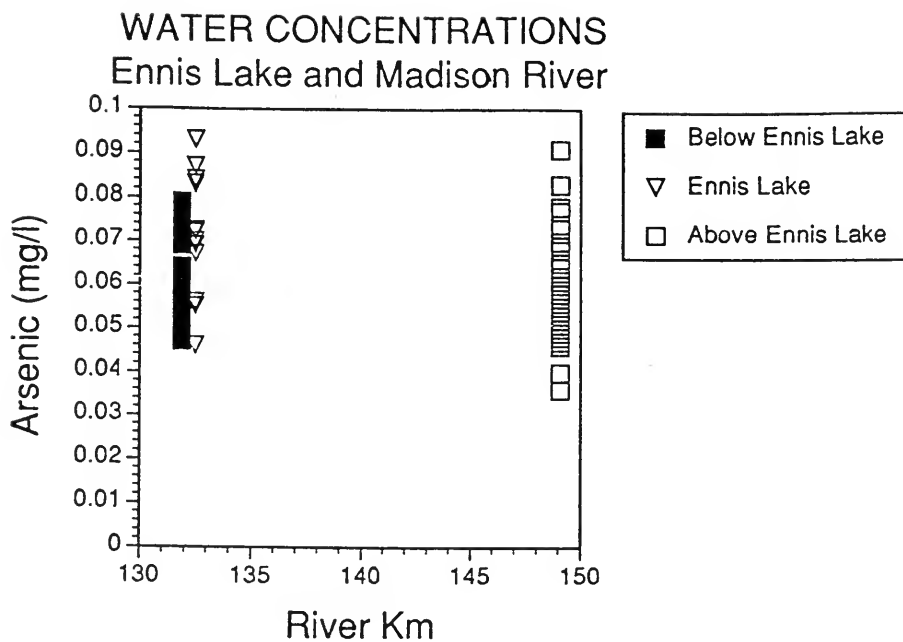


Figure 28. Relationship between dissolved arsenic concentrations from samples collected on the Madison River below Ennis Lake (site BER), above Ennis Lake (site AER), and Ennis Lake.

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Appendix. Table A. Carbonate, total, and organic carbon analysis for sediment samples (mg/kg). CF = Canyon Ferry Reservoir, OM and MO = Missouri River, TO = Toston Reservoir, GA = Gallatin River, JE = Jefferson River, MA and M = Madison River, EN = Ennis Lake, QL = Quake Lake, HL = Hebgen Lake, FH = Firehole River, G = Gibbon River, n = number of replicates, BD = Below Detection, L.O.D. = Limit of Detection.

n=	River Km.	Site	Carbonate Carbon	Standard Deviation
2	-0.8	CF1	5200	<50
2	-0.8	CF2	9400	400
2	-0.8	CF3	7100	50
2	-0.8	CF4	15500	350
2	-0.8	CF5	21600	100
2	-0.8	CF6	28300	150
2	0.0	*OM1	9200	<50
2	2.2	OM2	8900	50
2	3.5	OM3	10300	50
1	8.5	OM4	8800	0
2	13.6	OM5	9700	50
2	24.2	OM6	7600	<50
2	30.6	MO5	9700	<50
2	32.2	OM7	8900	<50
2	32.9	TO1	8600	<50
2	32.9	TO2	10700	50
4	32.9	TO3	10800	50
2	32.9	TO4	10800	50
2	32.9	TO5	11100	50
2	32.9	TO6	10200	<50
2	32.9	TO7	10000	<50
2	32.9	TO8	8900	50
2	32.9	TO9	10100	50
2	40	OM8	9900	100
2	42.4	OM9	9500	<50
2	49.6	OM10	10300	<50
2	53.3	OM11	10100	<50
2	64.2	OM12	11300	50
2	65.8	GA1	10800	50
2	65.8	GA2	11300	<50
2	65.8	GA3	10700	50
2	68	JE1	18300	50
2	68	JE2	19000	150
2	68	JE3	19400	200
2	68	JE4	18500	50
2	68	JE5	20800	<50

Appendix. Table A continued.

n=	River Km.	Site	Carbonate Carbon	Standard Deviation
2	68	JE6	17500	50
2	73.3	MA1	2200	50
2	85.9	MA2	1700	50
1	87.8	MA3	1600	0
2	96.8	MA4	1700	<50
2	99.7	MA5	1200	50
2	100.9	MA6	900	200
2	102.5	MA7	600	50
2	103.8	MA8	900	50
2	109.1	MA9	1800	100
2	115.1	MA10	1800	100
2	118.3	MA11	2100	<50
1	131.9	MA12	3000	0
2	132.5	EN1	2500	50
2	132.5	EN2	2300	<50
2	132.5	EN3	2300	300
2	132.5	EN4	5700	50
2	132.5	EN5	3300	50
2	132.5	EN6	3300	50
2	132.5	EN7	3100	<50
2	132.5	EN8	3100	<50
2	132.5	EN9	2900	200
2	132.5	EN10	2900	50
2	143.1	MA13	6100	100
2	143.8	MA14	6000	<50
2	144.7	MA15	6000	<50
2	145.5	MA16	6200	50
2	149.1	MA17	3400	100
1	153.2	MA18	5800	0
2	154.1	MA19	6600	400
1	198.8	MA21	5800	0
2	227.4	MA24	3500	50
2	228.3	MA25	1800	50
2	234.1	QL1	4000	100
2	234.1	QL2	4900	<50
2	234.1	QL3	700	<50
2	239.1	MA27	7900	<50
2	239.4	MA28	7700	<50
2	239.7	MA29	3700	150
2	239.9	MA30	9900	50
2	263.7	HL1	BD	0
2	263.7	HL2	1100	200

Appendix. Table A continued.

n=	River Km.	Site	Carbonate Carbon	Standard Deviation
2	263.7	HL3	100	<50
2	263.7	HL4	200	50
2	263.7	HL5	100	<50
2	263.7	HL6	BD	0
2	263.7	HL7	BD	0
2	263.7	HL8	BD	0
2	263.7	HL9	200	50
2	263.7	HL10	100	100
2	263.7	HL11	BD	0
1	263.7	HL12	BD	0
2	270	M7	100	<50
2	288.7	M6	200	<50
2	300.4	M1	100	<50
2	301.6	M2	100	<50
2	305.4	M3	100	<50
2	305.7	M4	100	<50
2	306.5	M5	100	<50
2	315	FH2	100	<50
2	327.5	FH1	300	<50
2	310.4	G2	200	<50
4	317.2	G1	100	50
		L.O.D.	100	

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n=	River Km.	Site	Total Carbon	Standard Deviation	Organic Carbon
3	-0.8	CF1	9100	300	3900
2	-0.8	CF2	15500	150	6100
2	-0.8	CF3	22000	350	14900
3	-0.8	CF4	39600	1150	24100
3	-0.8	CF5	69600	400	48000
2	-0.8	CF6	54000	1350	25700
2	0.0	*OM1	45800	150	36600
3	2.2	OM2	47200	2100	38300
2	3.5	OM3	40700	100	30400
2	8.5	OM4	37500	950	28700
2	13.6	OM5	44200	200	34500
2	24.2	OM6	37400	250	29800

Appendix. Table A continued.

n=	River Km.	Site	Total Carbon	Standard Deviation	Organic Carbon
2	30.6	MO5	36900	200	27200
2	32.2	OM7	45200	300	36300
3	32.9	TO1	28500	2450	19900
2	32.9	TO2	28500	350	17800
4	32.9	TO3	43200	50	32400
2	32.9	TO4	53400	1950	42600
2	32.9	TO5	51800	100	40700
2	32.9	TO6	51200	50	41000
2	32.9	TO7	50200	400	40200
2	32.9	TO8	50100	450	41200
2	32.9	TO9	55500	1050	45400
2	40	OM8	32000	800	22100
2	42.4	OM9	39500	500	30000
2	49.6	OM10	36700	1050	26400
3	53.3	OM11	34300	1850	24200
3	64.2	OM12	39300	4050	28000
2	65.8	GA1	40000	100	29200
2	65.8	GA2	39400	100	28100
2	65.8	GA3	30000	750	19300
2	68	JE1	47900	300	29600
2	68	JE2	54200	650	35200
3	68	JE3	53000	3150	33600
2	68	JE4	51700	200	33200
2	68	JE5	54400	1000	33600
2	68	JE6	49700	350	32200
2	73.3	MA1	29200	150	27000
2	85.9	MA2	41300	450	39600
2	87.8	MA3	42600	350	41000
2	96.8	MA4	24300	250	22600
2	99.7	MA5	24500	600	23300
2	100.9	MA6	21300	550	20400
2	102.5	MA7	16600	300	16000
2	103.8	MA8	15100	300	14200
2	109.1	MA9	23700	150	21900
2	115.1	MA10	21500	50	19700
2	118.3	MA11	33500	750	31400
2	131.9	MA12	37400	1250	34400
2	132.5	EN1	34300	50	31800
3	132.5	EN2	49000	1350	46700
2	132.5	EN3	37600	950	35300
2	132.5	EN4	21500	550	15800
2	132.5	EN5	30900	300	27600

Appendix. Table A continued.

n=	River Km.	Site	Total Carbon	Standard Deviation	Organic Carbon
2	132.5	EN6	32800	150	29500
2	132.5	EN7	28000	500	24900
2	132.5	EN8	24000	250	20900
2	132.5	EN9	30700	250	27800
2	132.5	EN10	34600	150	31700
2	143.1	MA13	31000	400	24900
2	143.8	MA14	31800	550	25800
2	144.7	MA15	30600	150	24600
2	145.5	MA16	29400	100	23200
2	149.1	MA17	45000	200	41600
2	153.2	MA18	33600	50	27800
1	154.1	MA19	32500	0	25900
1	198.8	MA21	36400	0	30600
2	227.4	MA24	29900	100	26400
2	228.3	MA25	19500	<50	17700
3	234.1	QL1	52700	750	48700
2	234.1	QL2	21700	200	16800
3	234.1	QL3	47600	950	46900
2	239.1	MA27	21700	100	13800
2	239.4	MA28	21600	50	13900
2	239.7	MA29	14600	300	10900
2	239.9	MA30	25000	100	15100
2	263.7	HL1	40200	6500	40200
2	263.7	HL2	24800	1250	23700
2	263.7	HL3	39800	250	39700
2	263.7	HL4	33000	300	32800
2	263.7	HL5	31300	600	31200
2	263.7	HL6	39300	400	39300
3	263.7	HL7	35700	2300	35700
3	263.7	HL8	33100	650	33100
2	263.7	HL9	34800	850	34600
2	263.7	HL10	28900	400	28800
2	263.7	HL11	31800	300	31800
2	263.7	HL12	46100	<50	46100
2	270	M7	21700	50	21600
2	288.7	M6	20600	100	20400
2	300.4	M1	17000	<50	16900
2	301.6	M2	22100	50	22000
4	305.4	M3	17400	650	17300
2	305.7	M4	20400	150	20300
2	306.5	M5	31300	100	31200
3	315	FH2	54800	1800	54700

Appendix. Table A continued.

n=	River Km.	Site	Total Carbon	Standard Deviation	Organic Carbon
3	327.5	FH1	46900	2950	46600
2	310.4	G2	37900	550	37700
4	317.2	G1	8200	300	8100
		L.O.D.	100		

\*River kilometers calculated from Rivermile Index of the Missouri River, Water Resources Division, Montana Department of Natural Resources and Conservation, January 1979. Site OM1 is located at "Highway 12 bridge near Townsend, MT. and U.S.G.S. gaging station #6-0570". River kilometers calculated using 1.609 km/mile.



Appendix. Table B. Dissolved metals analysis (mg/l) for water samples.

CF = Canyon Ferry Reservoir, OM and MO = Missouri River, TO = Toston Reservoir, GA = Gallatin River, JE = Jefferson River, MA and M = Madison River, EN = Ennis Lake, QL = Quake Lake, HL = Hebgen Lake, FH = Firehole River, G = Gibbon River, WC = Wolf Creek, CC = Cabin Creek, BD = Below Detection, L.O.D. = Limit of Detection, NM = No Measurement recorded.

River Km.	Site	Al	As	Ca	Fe
-0.8	CF	BD	BD	32.9	0.01
0.0	*MO1	BD	BD	58.46	0.054
24.2	MO2	BD	BD	42.78	0.04
27.8	MO3	BD	0.05	42.25	0.092
29	MO4	BD	BD	45.01	0.097
30.6	MO5	BD	BD	45.24	0.036
32.9	TO	0.035	0.053	76.6	0.116
49.6	MO6	0.05	BD	44.81	0.123
68	JE	BD	BD	58.09	0.016
73.3	MA1	BD	0.08	22.84	0.05
85.9	MA2	BD	0.08	22.38	0.052
87.8	MA3	0.04	0.07	27.13	0.056
96.8	MA4	BD	0.07	24.25	0.05
99.7	MA5	0.03	0.06	23.04	0.042
100.9	MA6	BD	0.07	23.9	0.033
102.5	MA7	BD	0.07	23.85	0.03
103.8	MA8	BD	0.07	26.38	0.033
109.1	MA9	0.04	0.06	23.54	0.057
115.1	MA10	0.03	0.07	23.9	0.058
118.3	MA11	BD	0.07	22.73	0.041
131.9	MA12	BD	0.08	25.1	0.032
132.5	EN	BD	0.12	37	0.06
143.1	MA13	BD	BD	31.97	0.02
143.8	MA14	BD	0.05	30.31	0.03
144.7	MA15	0.03	0.05	28.99	0.029
145.5	MA16	0.04	BD	44.72	0.026
149.1	MA17	BD	0.08	17.67	0.032
153.2	MA18	0.03	0.08	23.33	0.038
154.1	MA19	BD	0.07	26.31	0.103
163.7	MA20	0.04	0.08	19.82	0.037
198.3	WC	BD	BD	18.9	0.037
198.8	MA21	BD	0.09	15.21	0.044
208	MA22	0.04	0.07	14.95	0.086
213.9	MA23	0.03	0.1	14.67	0.103
227.4	MA24	BD	0.12	14.9	0.041
228.3	MA25	0.04	0.11	14.37	0.037

Appendix. Table B continued.

River Km.	Site	Al	As	Ca	Fe
234.1	QL	0.057	0.16	23.5	0.123
238.5	MA26	0.08	0.13	14.85	0.114
239.1	MA27	BD	0.13	16.43	0.071
239.4	MA28	0.05	0.12	15.27	0.068
239.7	MA29	0.05	0.11	21.27	0.111
239.9	MA30	0.04	0.13	21.46	0.068
240.1	CC	0.065	BD	77.7	0.039
263.7	HL	0.168	0.334	14.25	0.261
300.4	M1	0.154	0.2932	7.07	0.0513
315	FH2	0.0567	0.37	6.73	0.0214
327.5	FH1	0.041	0.157	4.42	0.0311
310.4	G2	0.3197	0.1597	8.96	0.1804
317.2	G1	0.303	0.18	8.13	0.2736
	L.O.D.	0.03	0.05	0.004	0.005

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River Km.	Site	Mn	Na	pH
-0.8	CF	0.003	19.5	8.1
0.0	MO1	0.152	36.7	7.8
24.2	MO2	0.012	26.9	8.3
27.8	MO3	0.014	26.4	7.9
29	MO4	0.015	27.3	7.9
30.6	MO5	0.02	28.7	7.7
32.9	TO	0.054	31.8	8.3
49.6	MO6	0.022	24.6	8.2
68	JE	0.006	21.25	8.3
73.3	MA1	0.008	35.3	8.3
85.9	MA2	0.005	34.3	8.2
87.8	MA3	0.015	31.3	8.1
96.8	MA4	0.004	32.9	7.9
99.7	MA5	0.004	30.6	8.1
100.9	MA6	0.004	31.9	8.1
102.5	MA7	0.004	31.5	8.1
103.8	MA8	0.012	29.2	8
109.1	MA9	0.008	26.6	8.2
115.1	MA10	0.005	34.9	8.2
118.3	MA11	0.005	34.5	8.3
131.9	MA12	0.005	30.8	8.3

Appendix. Table B continued.

River Km.	Site	Mn	Na	pH
132.5	EN	0.005	48.1	8.3
143.1	MA13	0.015	25.5	8.1
143.8	MA14	0.018	26.9	8.1
144.7	MA15	0.021	25.8	8.1
145.5	MA16	0.017	24.7	8
149.1	MA17	0.007	32.8	7.9
153.2	MA18	0.007	28.3	8.1
154.1	MA19	0.086	26.2	8.2
163.7	MA20	0.041	34.5	8.1
198.3	WC	0.002	8.4	NM
198.8	MA21	0.006	37	8.1
208	MA22	0.013	32	8
213.9	MA23	0.007	36.7	8
227.4	MA24	BD	43.3	8
228.3	MA25	0.003	42.6	8
234.1	QL	0.025	57.5	8.1
238.5	MA26	0.034	46.2	7.9
239.1	MA27	0.024	49.5	8
239.4	MA28	0.017	43.7	7.8
239.7	MA29	0.02	47.8	8.1
239.9	MA30	0.041	47	7.9
240.1	CC	0.003	9.7	NM
263.7	HL	0.027	104.76	7.4
300.4	M1	0.006	93.0214	7.5
315	FH2	BD	93	8.6
327.5	FH1	BD	51.6	8.1
310.4	G2	0.013	63.6667	6.9
317.2	G1	0.031	51.6	7.9
	L.O.D.	0.002	0.02	

\*River kilometers calculated from Rivermile Index of the Missouri River, Water Resources Division, Montana Department of Natural Resources and Conservation, January 1979. Site MO1 is located at "Highway 12 bridge near Townsend, MT. and U.S.G.S. gaging station #6-0570". River kilometers calculated using 1.609 km/mile.

Appendix. Table C. HCl-extractable metals analysis and standard deviations for sediment samples (mg/kg). CF = Canyon Ferry Reservoir, OM and MO = Missouri River, TO = Toston Reservoir, GA = Gallatin River, JE = Jefferson River, MA and M = Madison River, EN = Ennis Lake, QL = Quake Lake, HL = Hebgen Lake, FH = Firehole River, G = Gibbon River, n = number of replicate extractions, BD = Below Detection, L.O.D. = Limit of Detection.

n=	River Km.	Site	Al	Standard Deviation	As	Standard Deviation
3	-0.8	CF1	2562	200	4.34	0.95
3	-0.8	CF2	2032	142	11.58	0.95
4	-0.8	CF3	2969	162	15.96	0.53
3	-0.8	CF4	2393	167	25.58	1.46
3	-0.8	CF5	3270	196	32.15	0.13
4	-0.8	CF6	2648	85	18.58	0.68
5	0.0	*OM1	3868	69	31.75	0.75
3	2.2	OM2	3840	182	32.34	1.27
3	3.5	OM3	3815	153	27.16	0.53
4	8.5	OM4	4210	268	35.48	0.53
2	13.6	OM5	3821	84	22.88	0.64
3	24.2	OM6	3805	74	27.56	0.4
3	30.6	MO5	3976	165	27.77	0.64
2	32.2	OM7	5076	227	32.18	0.47
3	32.9	TO1	2758	100	6.85	0.78
4	32.9	TO2	2753	104	8.91	0.42
3	32.9	TO3	3540	293	13.92	0.29
3	32.9	TO4	4042	136	18.45	0.69
3	32.9	TO5	3500	203	17.28	0.47
3	32.9	TO6	3769	116	20.88	0.42
3	32.9	TO7	3474	63	21.27	0.5
4	32.9	TO8	3528	138	18.69	0.85
3	32.9	TO9	3888	95	17.61	0.52
3	40	OM8	4797	200	8.45	0.3
3	42.4	OM9	4405	85	24.27	0.8
4	49.6	OM10	3729	131	18.21	0.57
3	53.3	OM11	3934	41	7.5	0.91
2	64.2	OM12	4102	124	6.91	0.51
3	65.8	GA1	4340	211	9.01	0.12
3	65.8	GA2	4195	192	BD	0.26
3	65.8	GA3	4978	134	BD	0.59
3	68	JE1	3168	234	8.3	0.61
3	68	JE2	2970	53	6.94	0.39
3	68	JE3	2982	55	7.3	0.04
2	68	JE4	3331	53	6.22	0.55

Appendix. Table C continued.

n=	River Km.	Site	Al	Standard Deviation	As	Standard Deviation
3	68	JE5	3949	44	7.56	0.63
5	68	JE6	2832	159	6.49	1.45
2	73.3	MA1	3250	21	62.76	0.71
3	85.9	MA2	3693	72	82.34	0.18
2	87.8	MA3	3969	12	73.94	0.45
4	96.8	MA4	3347	63	43.25	0.54
4	99.7	MA5	3233	121	42.08	0.5
3	100.9	MA6	2929	75	31.56	1.02
3	102.5	MA7	3974	195	32.08	0.56
2	103.8	MA8	2713	14	21.72	0.34
3	109.1	MA9	3349	316	38.22	1.06
3	115.1	MA10	3060	29	59.35	0.38
3	118.3	MA11	4102	145	71.73	0.9
1	131.9	MA12	5451	0	63.78	0
4	132.5	EN1	3993	164	28.63	0.51
3	132.5	EN2	3642	161	27.87	0.79
3	132.5	EN3	3984	177	44.93	0.6
3	132.5	EN4	3863	102	25.67	0.77
3	132.5	EN5	3939	183	47.52	0.77
3	132.5	EN6	4428	132	56.8	3.84
4	132.5	EN7	4241	199	55.76	1.08
3	132.5	EN8	4094	188	40.49	0.85
3	132.5	EN9	5021	129	62.28	1.37
3	132.5	EN10	4345	306	50.83	0.94
3	143.1	MA13	3487	150	48.28	0.93
3	143.8	MA14	4162	251	43.94	1.47
3	144.7	MA15	3853	32	38.91	0.66
3	145.5	MA16	4210	19	39.69	0.66
3	149.1	MA17	3460	168	74.51	1.82
2	153.2	MA18	4370	153	46.27	0.3
2	154.1	MA19	3968	4	80.73	0.16
1	163.7	MA20	4096	0	91.83	0
3	198.8	MA21	3677	138	137.95	0.87
1	208	MA22	6038	0	95.08	0
1	213.9	MA23	4261	0	66.15	0
3	227.4	MA24	4642	157	128.52	0.3
3	228.3	MA25	4944	461	65.04	0.55
3	234.1	QL1	3137	76	74.43	1.92
3	234.1	QL2	3834	101	20.12	0.52

Appendix. Table C continued.

n=	River Km.	Site	Al	Standard Deviation	As	Standard Deviation
3	234.1	QL3	3659	84	30.79	0.14
3	239.1	MA27	2334	85	45.26	0.16
3	239.4	MA28	2173	25	48.43	0.25
3	239.7	MA29	2436	172	51.66	1.5
4	239.9	MA30	2440	117	30.37	0.75
3	263.7	HL1	2678	11	59.42	0.54
3	263.7	HL2	1710	117	38.06	2.44
3	263.7	HL3	3933	97	95.72	0.31
3	263.7	HL4	3855	87	103.58	0.52
3	263.7	HL5	3195	125	64.55	1.83
3	263.7	HL6	3191	3	82.7	1.63
4	263.7	HL7	3162	65	48.87	1.44
4	263.7	HL8	2802	94	64.5	0.84
3	263.7	HL9	3596	163	93.75	3.84
3	263.7	HL10	4603	114	90.67	1.6
1	263.7	HL11	4774	0	110.18	0
3	263.7	HL12	4300	57	135.53	0.16
2	270	M7	2662	5	27.69	0
4	288.7	M6	2565	33	24.38	3.7
2	300.4	M1	2948	5	47.14	1.43
3	301.6	M2	2726	19	57.21	0.46
3	305.4	M3	2628	37	32.65	1.75
2	305.7	M4	3111	44	45.15	0.95
2	306.5	M5	4394	29	62.95	1.76
3	315	FH2	3569	98	24.51	3.37
2	327.5	FH1	3698	53	22.67	2.23
5	310.4	G2	5472	105	174.69	2.47
2	317.2	G1	733	38	29.57	1.74
		L.O.D.	3		4.00	

Appendix. Table C continued.

n=	River Km.	Site	Fe	Standard Deviation	Mn	Standard Deviation
3	-0.8	CF1	3792	295	214.3	3.5
3	-0.8	CF2	2865	189	253.7	20.2
4	-0.8	CF3	4685	219	397.4	5.7
3	-0.8	CF4	4935	299	954.3	48.6
3	-0.8	CF5	7012	295	1319.7	8.6
4	-0.8	CF6	4486	125	909.3	8.2
5	0.0	*OM1	6233	98	1150.7	3.8
3	2.2	OM2	5916	262	1406	3.8
3	3.5	OM3	5326	203	711.6	5.4
4	8.5	OM4	7450	412	554.2	5.7
2	13.6	OM5	6056	118	670.8	3.7
3	24.2	OM6	5947	97	507.6	1.2
3	30.6	OM5	6072	215	722.7	6.3
2	32.2	OM7	8020	335	580.1	1.4
3	32.9	TO1	4970	155	422.4	7.4
4	32.9	TO2	4840	163	479.7	7
3	32.9	TO3	6023	422	642.1	6.7
3	32.9	TO4	6820	164	643.6	4
3	32.9	TO5	5958	261	634.3	7.2
3	32.9	TO6	6687	155	601.3	9.3
3	32.9	TO7	6150	89	480.9	0.2
4	32.9	TO8	6280	191	401.7	3.9
3	32.9	TO9	6678	123	660.8	1.2
3	40	OM8	7458	334	384.3	2.7
3	42.4	OM9	7081	136	425.9	2.2
4	49.6	OM10	5465	200	656.4	7.3
3	53.3	OM11	6075	52	190.5	2.1
2	64.2	OM12	5405	122	317.7	1.3
3	65.8	GA1	5843	266	375.1	3.6
3	65.8	GA2	5192	242	334.2	1.7
3	65.8	GA3	6037	182	466.9	4.2
3	68	JE1	5267	335	1117	23
3	68	JE2	5302	33	1274.7	4.2
3	68	JE3	5303	82	1439	7.2
2	68	JE4	5689	97	954.7	8.9
3	68	JE5	6419	44	1240.7	3.5
5	68	JE6	4960	215	1108.1	10
2	73.3	MA1	6395	18	965.4	8.2
3	85.9	MA2	8159	133	718.1	3.8

Appendix. Table C continued.

n=	River Km.	Site	Fe	Standard Deviation	Mn	Standard Deviation
2	87.8	MA3	8054	45	116.8	2.6
4	96.8	MA4	6315	114	803.8	3.3
4	99.7	MA5	6086	184	553.9	5.6
3	100.9	MA6	5502	104	351.9	5.5
3	102.5	MA7	6332	321	475.5	14.7
2	103.8	MA8	4273	29	328.8	0
3	109.1	MA9	6477	521	657.8	6.4
3	115.1	MA10	7031	73	744.3	4.2
3	118.3	MA11	8846	291	985.3	8
1	131.9	MA12	10597	0	2274.5	0
4	132.5	EN1	9227	334	1127.1	7.4
3	132.5	EN2	9143	386	1252.7	12.6
3	132.5	EN3	9670	335	873.1	14.2
3	132.5	EN4	8648	328	824.8	36.7
3	132.5	EN5	10336	431	1165.9	16.3
3	132.5	EN6	10795	301	1377.4	68.7
4	132.5	EN7	9864	443	1661.6	35.7
3	132.5	EN8	9328	405	1199.5	18.7
3	132.5	EN9	11465	273	2202.3	57.2
3	132.5	EN10	9939	636	1330.7	13.6
3	143.1	MA13	7103	232	396.2	0.9
3	143.8	MA14	7718	380	436.4	14.1
3	144.7	MA15	7345	60	294.1	0.8
3	145.5	MA16	7599	100	487.4	6.5
3	149.1	MA17	7234	267	275.4	2.7
2	153.2	MA18	7037	204	660.5	0.7
2	154.1	MA19	8568	16	563.5	3.7
1	163.7	MA20	9669	0	469	0
3	198.8	MA21	9994	254	1739	10.6
1	208	MA22	21421	0	952.7	0
1	213.9	MA23	10602	0	4420.6	0
3	227.4	MA24	10487	272	8718.8	87.3
3	228.3	MA25	10888	857	409.1	8
3	234.1	QL1	10012	259	1114.2	13.6
3	234.1	QL2	12317	179	1319.4	2.1
3	234.1	QL3	9008	165	456.8	13.3
3	239.1	MA27	5639	96	514.9	2.4
3	239.4	MA28	5224	36	709.4	1.7
3	239.7	MA29	6275	368	617.5	20.9



Appendix. Table C continued.

n=	River Km.	Site	Fe	Standard Deviation	Mn	Standard Deviation
4	239.9	MA30	4842	183	1010.2	18.1
3	263.7	HL1	1930	10	296.2	4.5
3	263.7	HL2	1578	75	240	17.5
3	263.7	HL3	3082	94	469.8	8.6
3	263.7	HL4	3036	59	466.9	7.8
3	263.7	HL5	3038	94	454.6	10.6
3	263.7	HL6	2383	18	241.1	1.6
4	263.7	HL7	1893	25	116.1	3.1
4	263.7	HL8	2327	94	215.2	2.8
3	263.7	HL9	5508	196	534.4	21.6
3	263.7	HL10	6033	135	511.3	12
1	263.7	HL11	7836	0	549.9	0
3	263.7	HL12	8804	166	1601.9	15.5
2	270	M7	1906	26	199.5	10.8
4	288.7	M6	1934	33	405.2	18.4
2	300.4	M1	2119	12	231.4	2.9
3	301.6	M2	2307	15	182.3	3.7
3	305.4	M3	2228	41	187	11.1
2	305.7	M4	2521	15	333.9	1.5
2	306.5	M5	3298	11	454.1	1.2
3	315	FH2	4306	70	1203.6	11.7
2	327.5	FH1	4029	81	1949.3	22.2
5	310.4	G2	5521	59	1152.8	6.8
2	317.2	G1	1008	40	190.7	7
		L.O.D.	0.4		0.2	

Appendix. Table C continued.

n=	River Km.	Site	Ca	Standard Deviation	Na	Standard Deviation
3	-0.8	CF1	17578	161	49.54	2.58
3	-0.8	CF2	28367	2520	35.83	3.44
4	-0.8	CF3	24729	98	56.68	3.42
3	-0.8	CF4	52353	2519	83.16	6.65
2	-0.8	CF5	72771	239	67.09	1.38
3	-0.8	CF6	87682	1743	65.29	0.87
3	0.0	*OM1	34851	79	93.73	3.55
3	2.2	OM2	31275	138	110.91	4.15
3	3.5	OM3	34779	236	103.36	5.59
2	8.5	OM4	32328	68	89.44	1.57
2	13.6	OM5	33976	111	102.21	1.81
3	24.2	OM6	29692	45	121.97	2.79
3	30.6	MO5	32787	405	98.94	4.31
2	32.2	OM7	31818	131	145.5	2.27
3	32.9	TO1	30010	54	46.12	6.58
3	32.9	TO2	33391	393	41.91	1.73
3	32.9	TO3	36764	257	50.4	4.61
3	32.9	TO4	36332	174	55.88	1.17
3	32.9	TO5	36009	644	64.33	3.94
3	32.9	TO6	34967	650	62.14	2.27
3	32.9	TO7	33297	1719	51.83	3.2
3	32.9	TO8	30981	291	61.04	4.31
3	32.9	TO9	34619	102	60.79	1.63
3	40	OM8	33896	120	61.48	1.43
3	42.4	OM9	33345	889	81.91	2.17
2	49.6	OM10	35786	149	87.63	4.06
3	53.3	OM11	33360	351	48.33	1.98
2	64.2	OM12	37744	112	70.22	4.93
3	65.8	GA1	36831	1020	68.11	2.8
3	65.8	GA2	37986	1418	62.26	3.06
3	65.8	GA3	38047	261	48.92	1.32
2	68	JE1	59959	590	77.64	2.67
3	68	JE2	61274	302	62.1	3.8
2	68	JE3	62329	883	74.82	4.13
2	68	JE4	59448	201	64.94	5.62
3	68	JE5	67106	628	86.21	2.25
3	68	JE6	55637	1027	66.05	8.13
2	73.3	MA1	11032	25	124.7	5.31
3	85.9	MA2	9939	55	127.64	2.96

Appendix. Table C continued.

n=	River Km.	Site	Ca	Standard Deviation	Na	Standard Deviation
2	87.8	MA3	8480	41	138.95	3.57
4	96.8	MA4	8947	38	98.88	0.43
4	99.7	MA5	8032	166	113.53	20.15
3	100.9	MA6	7916	66	93.65	3.33
3	102.5	MA7	7436	86	120.19	3.79
2	103.8	MA8	7180	62	84.69	0.47
3	109.1	MA9	8787	43	85.74	3.06
3	115.1	MA10	10944	88	102.52	1.5
3	118.3	MA11	9957	81	133.91	4.5
1	131.9	MA12	12468	0	135.86	0
4	132.5	EN1	10221	63	81.61	2.56
3	132.5	EN2	10550	126	48.57	1.8
3	132.5	EN3	9312	66	89.65	1.66
3	132.5	EN4	18479	435	91.33	0.29
3	132.5	EN5	12394	72	102.08	3.54
3	132.5	EN6	11563	167	82.32	1.72
4	132.5	EN7	11510	80	84.13	1.92
3	132.5	EN8	11020	21	97.43	2.09
3	132.5	EN9	11693	66	101.75	1.07
3	132.5	EN10	11403	59	84.72	4.59
3	143.1	MA13	17899	32	67.17	2.02
3	143.8	MA14	17556	61	104.86	0.65
3	144.7	MA15	18494	79	94.06	4.75
3	145.5	MA16	18899	236	103.57	3.83
3	149.1	MA17	11684	32	135.28	2.67
2	153.2	MA18	19009	114	128.87	1.64
2	154.1	MA19	20421	161	95.92	1.78
1	163.7	MA20	16385	0	117.94	0
3	198.8	MA21	15393	28	107.86	1.63
1	208	MA22	13121	0	98.88	0
1	213.9	MA23	12409	0	177.92	0
3	227.4	MA24	10719	7	179.44	5.93
3	228.3	MA25	7483	41	104.84	0.84
3	234.1	QL1	11937	174	79.6	1.09
3	234.1	QL2	13519	35	67.52	1.66
3	234.1	QL3	5860	143	39.52	3.45
3	239.1	MA27	21951	136	136.83	2.29
3	239.4	MA28	22419	77	153.18	1.74
3	239.7	MA29	12737	49	107.65	2.88

Appendix. Table C continued.

n=	River Km.	Site	Ca	Standard Deviation	Na	Standard Deviation
4	239.9	MA30	30109	293	127.32	3.22
3	263.7	HL1	2441	27	169.97	8.89
3	263.7	HL2	1846	50	88.56	4.52
3	263.7	HL3	3154	35	212.76	4.72
3	263.7	HL4	2918	29	251.07	10.77
3	263.7	HL5	2353	51	181.11	13.56
3	263.7	HL6	2638	5	141.47	5.77
4	263.7	HL7	2590	41	92.15	5.96
4	263.7	HL8	2010	22	89.82	2.08
3	263.7	HL9	3108	107	207.22	3.73
3	263.7	HL10	3443	70	215.12	12.21
1	263.7	HL11	3497	0	277.05	0
3	263.7	HL12	4002	90	177.52	1.1
2	270	M7	2010	10	260.51	71.79
4	288.7	M6	1840	28	281.88	61.59
2	300.4	M1	1790	19	414.76	70
3	301.6	M2	2023	23	327.44	73.49
3	305.4	M3	1618	25	296.89	67.56
2	305.7	M4	2116	0	283.11	64.44
2	306.5	M5	2906	12	439.41	87.65
3	315	FH2	3815	55	502.31	105.38
2	327.5	FH1	2978	18	260.44	63.11
5	310.4	G2	3252	26	339.12	69.49
2	317.2	G1	614	17	94.78	36.81
		L.O.D.	0.32		1.6	

\*River kilometers calculated from Rivermile Index of the Missouri River, Water Resources Division, Montana Department of Natural Resources and Conservation, January 1979. Site OM1 is located at "Highway 12 bridge near Townsend, MT. and U.S.G.S. gaging station #6-0570". River kilometers calculated using 1.609 km/mile.

Appendix. Table D. HCl-extractable metals analysis (mg/kg) and standard deviations for Ennis Lake sediment core samples and Madison River sediment samples collected above Ennis Lake. L.O.D. = Limit of Detection, n = number of replicate extracts, \* = river kilometer of Madison River site.

n =	Depth Interval (cm)	Site	Al	Standard Deviation	As	Standard Deviation
3	0 - 10	EN1B	4194	147	73.1	3.7
4	10 - 20	EN1B	4623	57	29.32	1.05
4	20 - 30	EN1B	4619	175	28.13	0.91
4	30 - 40	EN1B	4235	121	29.31	0.48
3	40 - 46	EN1B	4032	147	30.43	0.61
3	0 - 10	EN2B	4431	206	15.91	0.9
4	10 - 20	EN2B	4327	101	15.96	0.81
3	20 - 30	EN2B	4534	55	16.02	0.13
3	30 - 38	EN2B	3460	182	13.96	0.73
4	0 - 10	EN3B	4050	35	38.46	0.73
4	10 - 20	EN3B	4171	128	29.72	0.64
4	20 - 25	EN3B	4164	247	28.95	1.59
4	0 - 10	EN4B	4843	84	38.21	1.03
4	10 - 20	EN4B	4521	163	29.51	0.79
4	20 - 21	EN4B	4468	144	18.31	0.73
4	0 - 10	EN5B	4802	172	33.1	1.26
4	0 - 10	EN6B	5206	222	33.07	1.3
3	10 - 17	EN6B	5044	47	27.83	0.49
4	0 - 10	EN7B	4735	232	37.61	1.57
3	10 - 17	EN7B	4669	239	47.65	0.73
4	0 - 10	EN8B	3389	120	32.21	0.82
3	10 - 20	EN8B	3369	235	29.27	1.07
4	0 - 10	EN9B	4707	280	43.48	5.47
3	10 - 20	EN9B	5200	218	26.51	1.42
3	20 - 30	EN9B	4654	188	33.16	0.55
4	30 - 40	EN9B	4209	95	30.41	0.31
4	40 - 50	EN9B	4128	60	31.67	0.6
3	< 10	EN10B	3576	182	19.67	0.73
3	< 10	EN13	3423	323	11.53	0.45
3	*km 143.1	MA13B	3639	77.81	16.29	0.65
3	*km 143.8	MA14B	3764	45.41	28.07	1.03
3	*km 144.7	MA15B	2976	91.07	17.55	0.58
3	*km 145.5	MA16B	3454	112.35	15.39	0.73
		L.O.D.	3		4	

Appendix. Table D continued.

n =	Depth Interval (cm)	Site	Ca	Standard Deviation	Fe	Standard Deviation
3	0 - 10	EN1B	10686	28	10546	221
4	10 - 20	EN1B	10022	119	11488	34
4	20 - 30	EN1B	9897	37	11518	395
4	30 - 40	EN1B	9882	35	10296	280
3	40 - 46	EN1B	9680	41	9228	270
3	0 - 10	EN2B	17949	142	8823	348
4	10 - 20	EN2B	16251	152	8598	191
3	20 - 30	EN2B	13824	233	9119	115
3	30 - 38	EN2B	10070	381	7507	322
4	0 - 10	EN3B	9069	74	9922	105
4	10 - 20	EN3B	7510	58	8285	233
4	20 - 25	EN3B	7776	77	6827	375
4	0 - 10	EN4B	9046	102	10205	156
4	10 - 20	EN4B	8421	63	7709	204
4	20 - 21	EN4B	7998	24	7192	217
4	0 - 10	EN5B	10618	27	10865	384
4	0 - 10	EN6B	0	0	9230	390
3	10 - 17	EN6B	0	0	8960	82
4	0 - 10	EN7B	12222	74	10958	460
3	10 - 17	EN7B	22491	241	9311	480
4	0 - 10	EN8B	9736	119	7562	259
3	10 - 20	EN8B	12804	74	6906	297
4	0 - 10	EN9B	11187	56	11024	580
3	10 - 20	EN9B	11093	49	12348	427
3	20 - 30	EN9B	10902	46	11427	386
4	30 - 40	EN9B	10297	99	10012	121
4	40 - 50	EN9B	10130	109	9928	121
3	< 10	EN10B	14545	1540	6159	108
3	< 10	EN13	4778	122	6922	606
3	*km 143.1	MA13B	21298	106.06	6055	135.23
3	*km 143.8	MA14B	21416	234.17	6600	64.69
3	*km 144.7	MA15B	22588	97.09	5185	164.84
3	*km 145.5	MA16B	22908	193.03	5992	193.02
		L.O.D.	0.32		0.4	

Appendix. Table E. Concentrations (mg/l), pH, and (standard deviations) for Ennis Lake and Madison River water samples. L.O.D. = Limit of Detection, BD = Below Detection.

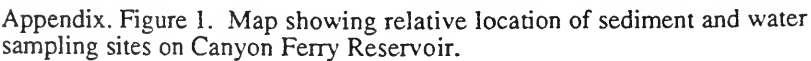
n=	Site	*Al	As	Ca	Fe
44	BER	0.071 (0.027)	0.066 (0.015)	21 (2.9)	0.035 (0.016)
13	Ennis Lake	BD	0.071 (0.013)	22.4 (2.4)	0.008 (0.009)
50	AER	0.045 (0.014)	0.06 (0.011)	16.2 (0.73)	0.038 (0.009)
	L.O.D.	0.03	0.05	0.004	0.005

\*n = 42 and 46 for sites BER and AER, respectively.

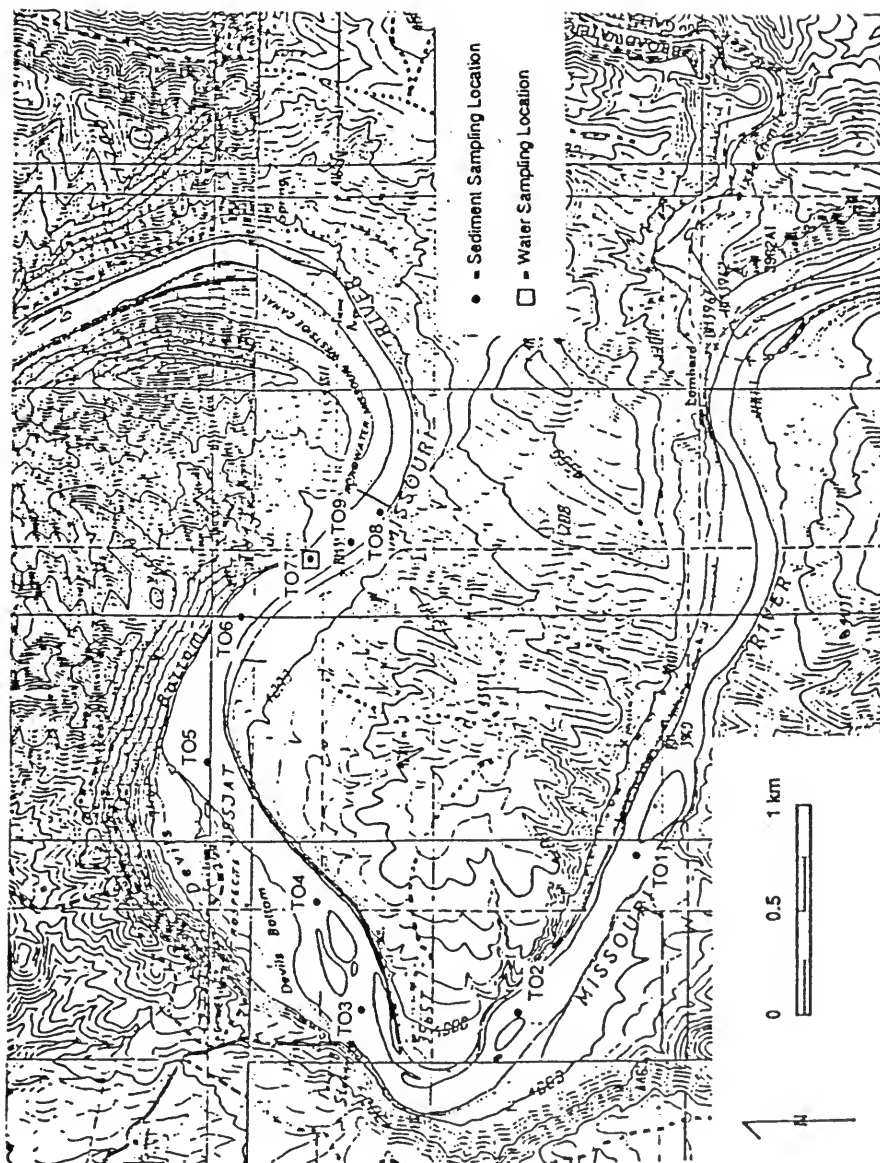
n=	Site	Mn	Na	n= (for pH)	pH
44	BER	0.004 (0.001)	17.4 (8.4)	23	8.4 (0.04)
13	Ennis Lake	0.013 (0.012)	13.2 (1.2)	15	8.6 (0.25)
50	AER	0.006 (0.002)	13 (0.47)	23	8.4 (0.18)
	L.O.D.	0.002	0.02		

Appendix. Table F. Results of hypolimnion tests conducted on Ennis Lake.

Site	Sample Depth (Meters)	Temperature (°C)	Site	Sample Depth (Meters)	Temperature (°C)
HPT1	0.5	18.7	HPT4	0.5	18.7
	3.7	19.4		3.7	19.2
HPT2	0.5	18.7	HPT5	1.0	22.0
	3.9	19.6		8.5	21.9
HPT3	0.5	18.7			
	4.1	19.3			







Appendix. Figure 2. Map showing relative location of sediment and water sampling sites on Toston Reservoir.





